CURSILLOS Y CONFERENCIAS

Instituto de Investigaciones Geológicas
"Lucas Mallada"
C.S.I.C. (España)

CURSILLOS Y CONFERENCIAS

DEL

INSTITUTO "LUCAS MALLADA"

FASCICULO VIII

Trabajos presentados en el Simposium sobre Feldespatos
organizado por la Asociación Internacional de Mineralogía
Copenhague, Agosto 1960

INDICE

Anorthite and Plagioclases

PREFACIO

En este volumen se han reunido todas las comunicaciones que se presentaron en el Simposium sobre Fedespatos que tuvo lugar en Copenhague en 1960 durante la reunión de la Asociación Internacional de Mineralogía. En los casos en que no se recibieron los manuscritos se han incluido los resúmenes de los correspondientes trabajos tal como estaban impresos en el Programa de le Reunión de Copenhague.

Se han añadido además dos trabajos, uno de GOLDSMITH y LAVES, otro de KARAMATA, que no fueron incluidos en el programa de la Reunión por dificultades de falta de tiempo dentro de los planes originales de la misma. No obstante, como ambos trabajos ya estaban redactados, se pudo disponer de tiempo para leer uno de ellos, el de KARAMATA; como el tema del trabajo de GOLDSMITH y LAVES encaja además en el lema de este Simposium, hemos considerado justificado incluirle también.

También por falta de tiempo no fue posible establecer discusiones sobre todos los temas tratados, y por ello se han preparado después comentarios algo más extensos, especialmente por DIETRICH y por LAVES y GOLDSMITH; como estos comentarios se refieren a varios de los temas tratados en diferentes trabajos, se han impreso separadamente. Por último, se ha considerado útil incluir, al final de los trabajos, una lista bibliográfica de los trabajos en que se estudian las estructuras de los feldespatos mediante rayos X, especialmente de los que determinan con exactitud las posiciones de los átomos. Esta bibliografía ha sido amablemente facilitada por la Dra. MEGAW.

En el capítulo de discusiones que acompaña al final de cada trabajo se han incluido las que fueron entregadas al Director del Simposium. También aparecen algunas más que fueron preparadas después que se dispuso de los textos finales de los manuscritos. Con objeto de que este aspecto de la discusión fuera lo más fructífero posible se anunció en la apertura del Simposium que se facilitarían fotocopias de estos manuscritos a todos aquellos interesados en su discusión. Leyendo las discusiones, es evidente que existen algunas importantes diferencias de opinión respecto a algunos puntos; esperamos que esto anime y estimule hacia nuevas investigaciones, especialmente hacia aquellas de carácter experimental.

F. LAVES.
(Director del Simposium.)

J. M. FÚSTER.
(Editor del Instituto "Lucas Mallada".)

PREFACE

All papers of the Feldspar-Symposium presented at the Copenhagen Meeting are included in this volume. In the cases where no manuscript was received only the abstract of the Copenhagen program has been reprinted here.

Two papers (by GOLDSMITH and LAVES and by KARAMATA) have been included here although they were not on the Copenhagen program as the original schedule did not allow an allotment of time for them. However, as two other papers had been withdrawn, the KARAMATA paper could be presented orally. As the subject of the GOLDSMITH-LAVES paper fits well into the theme of the Symposium its inclusion here appears to be justified.

Owing to lack of time, it was not possible to have full discussions on a number of points. Some rather extensive comments (by DIETRICH and by LAVES and GOLDSMITH) were prepared later. These are printed separately as their subject covers several papers.

A list of papers which deal with X-ray work on feldspar structures with special emphasis on the determination of exact atomic positions has been kindly prepared by Dr. MEGAW and is printed at the end of this volume.

Contribution to the discussion which were submitted to the chairman are included. The discussion also includes various comments which were prepared after the final texts of the manuscripts became available. (It was announced at the opening of the Symposium that microphotographs of the final manuscripts would be distributed on request.) From the discussion, it is clear that certain important differences of opinion occur and it is hoped that these may stimulate and encourage new researches, especially along experimental lines.

F. LAVES.
(Chairman of the Symposium.)

J. M. FÚSTER.
(Editor of Instituto "Lucas Mallada".)

Project of a new general catalogue of data for the determination of plagioclases by the universal-stage method

by C. Burri, R. L. Parker and E. Wenk.
Swiss Federal Institute of Technology and University of Basle.

ABSTRACT (*)

As will be generally conceded by all interested in the optical study of plagioclase feldspars by the Fedorow methods, the stereograms available at the present time for the determination of these minerals are no longer up-to-date. A project has, therefore, been started by the authors to collect and critically revise all published data on the optical orientation of plagioclases with a view to construct new stereograms. The optical orientation of a number of plagioclases of known chemical composition has been newly determined and these include both low- and high-temperature forms. An urgent appeal is addressed to all interested in this matter to supply the authors with reprints of papers bearing on the subject, especially when these are contained in periodicals of limited circulation. Any specimens suitable for chemical and optical study that could be given to the authors would be highly appreciated and would help to make the new stereograms as efficient a tool as possible.

(*) Reprinted from the program, distributed in Copenhagen, August 1960, as no manuscript was received.

The feldspar lattices as solvents of foreign ions

by Tom. F. W. Barth.

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ABSTRACT

The crystal lattices of the rock-making feldspars are of two slightly different types: the lattice of the plagio-clases, and the lattice of the alkali feldspars. Whitin a limited range of composition soda is distributed between the two lattices with a rather constant ratio of distribution (at constant temperature). The change of the coefficient of distribution with temperature can be expressed by an equation presented in the paper.

This constitutes a geological thermometer of great importance, making possible the determination of the tempera-ture of (re)crystallization of a given rock. A series of rocks may in this way be arranged according to increasing (or decreasing) temperature. Such arrangements are highly important, indeed, they form a necessary pre-requisite for the understanding of certain fundamental crystallo-chemical and geochemical relations of the feldspar minerals.

In addition the distribution of Sr, Ba, Pb, Rb, Cu is also discussed.

I. INTRODUCTION.

The rock-making feldspars are composed of three chief molecules, Or, Ab, and An, i.e. $KAlSi_3O_8$, $NaAlSi_3O_8$ and $CaAl_2O_8$ respectively.

However, solid solutions between the large cations are restrited to Na-Ca feldspars (= plagioclases) and Na-K feldspars (= alkalifeldspars). Chemically there are therefore two chief variants of structure: the structure of the plagioclases and the structure of the alkalifeldspars.

In many of the usual rock types these two structure variants coexist and serve as solid solvents for more or less the same elements.

A major element which enters both into plagio-clases and into alkali feldspars is soda itself. Let x_1 be the concentration of Na in alkali feldspar, and x_2 the concentration of Na in plagioclase, P = pressure, T = temperature. At equilibrium any of the varia-bles can be represented as a function of the other three, therefore there exists a characteristic relation that may be expressed as follows:

$$\Phi (x_1, x_2, P, T) = O$$

The effect of pressure seems to be of less impor-tance than is that of temperature and of composition, and will therefore, in this first approximation be neglected.

It has been shown (BARTH, 1956) that for natural plagioclase in the composition range $An_5 — An_{35}$ the following relation is approximately correct:

$$\frac{\text{mole fraction of Ab in alkali feldspar}}{\text{mole fraction of Ab plagioclase}} = \frac{x_1}{x_2} = k_T$$

where k_T, the coefficient of distribution, is constant at constant temperature. See fig. 1 A: at each temp-

erature the tie-lines are parallel (on a logarithmic scale).

Fig. 1 B shows how soda is distributed between alkali feldspar and an aqueous solution of alkali chloride at 600°. In solutions of less than 50 mol % Na^+/total alkali ions the tie-lines are approximately parallel, again indicating that, within this composition range, the coefficient of distribution is constant.
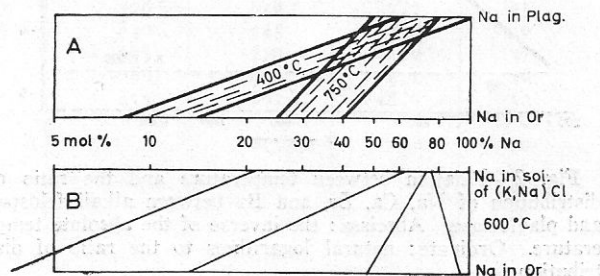
Fig. 1.—A. Distribution of Na (in terms of Ab molecules) between an orthoclase lattice and a coexisting plagioclase lattice at 400° C. and at 750° C. (Data from BARTH, 1956.)

B. Distribution of Na between an orthoclase lattice and a 2-molecular solution of $NaCl + KCl$ at 600° C. (Data from ORVILLE, 1958.)

Fig. 1 A shows furthermore that the coefficient of distribution is different at different temperatures. The theoretical variation of the coefficient with abso-lute temperature, T, is given by the equation

$$k_T = k_o \, e^{-\frac{\Delta E}{RT}}$$

or

$$\ln k_T = -\frac{\Delta E}{T} \cdot \frac{1}{R} + \ln k_o$$

where ΔE is the difference in lattice energy between

one mole of albite dissolved in alkali feldspar and dissolved in plagioclase; k_0 is the coefficient in a notional standard state.

Plotting this equation as a function of $1/T$ says that the result should be a straight line whose slope is proportional to $-\Delta E$. How well this is fulfilled is shown by the curve for Na in fig. 2. This curve approaches that of a straight line; it gives us the relation between temperature and the compositions of
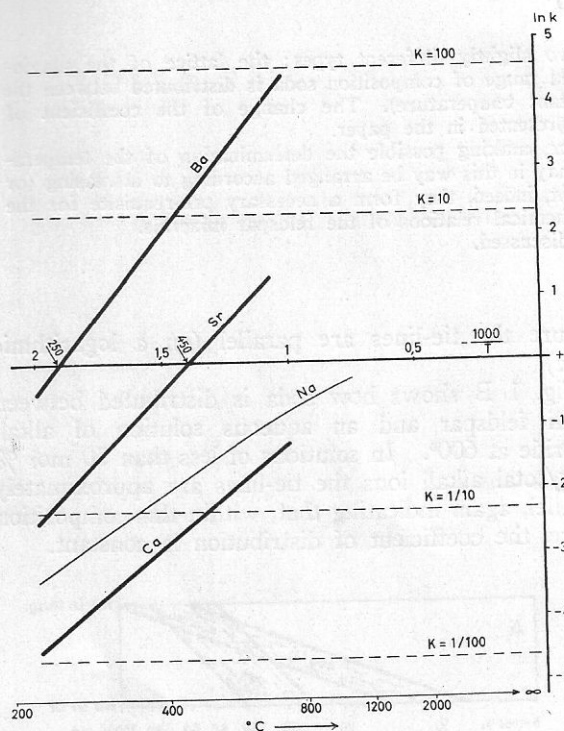
Fig. 2.—Relation between temperature and the ratio of distribution of Na, Ca, Sr, and Ba between alkali feldspar and plagioclase. Abscissa: the inverse of the absolute temperature. Ordinate: natural logarithms to the ratio of distribution.

the two feldspar phases in a rock; it is a geological thermometer of great importance. (For further discussion, see BARTH, 1956.)

A series of rocks may now be arranged according to increasing (or decreasing) temperatures. Such arrangements are highly important; indeed, only in this way is it possible to investigate into certain fundamental crystallochemical and geochemical relations of the natural feldspars.

II. THE CHEMICAL DATA.

In a notable paper on the chemical petrology of the metamorphic complex north of Lofoten (Northern Norway), HEIER (1960) has given some very interesting chemical data on a number of coexisting feldspar

phases. In addition to K, Na and Ca he has determined the amounts of Sr, Ba, Li, Rb, Cu and Pb. Additional pertinent data on several feldspar pairs have been published by HOWIE (1955). See table 1.

As explained in the introduction it is possible, on the basis of the Na-determinations, to calculate the feldspar crystallization temperatures of the several rocks. The temperatures thus determined fix the positions of the rocks on the horizontal axis of fig. 2. The curves designated Ca, Sr, and Ba are drawn after HEIER's data and illustrate the distribution of these elements between coexisting alkali feldspar and plagioclase at temperatures ranging from 200° to 700° C. The distribution of the other elements, Li, Rb, Cu, and Pb show no relation to temperature.

III. THE SYSTEMATIC DISTRIBUTION OF STRONTIUM AND BARIUM, VS. THE UNSYSTEMATIC DISTRIBUTION OF LITHIUM, RUBIDIUM, COPPER, AND LEAD.

It is of more than ordinary interest that the curves for Ca, Sr, and Ba thus constructed approximate straight lines. This was not be expected, for both alkali feldspars and plagioclases are mixed crystals and the lattice geometry changes notably with changing composition. The significance of these curves is therefore absolutely restricted to the limited range of the chemical composition of the feldspars investigated by HEIER; viz: Plagioclases in the range 20 An-40 An, and alkali feldspars with 75-90 K-feldspar.

Although it must be emphasized that some of the temperature calculations are rather uncertain, that the number of chemical determinations are small, and that the individual plots allow the lines to be drawn slightly curved in different directions, the trend of the curves are unmistakable. For Ca, Sr, and Ba there is a clear and regular increase of the coefficient of distribution with temperature, and the increase is less for Ca than for Ba, while Sr lies in between.

For eight pairs of feldspars investigated by OFTEDAL (1958) the k-values for Sr and Ba seem to lie systematically lower; but data published by HOWIE (1955) are in qualitative agreement with the curves.

Referring again to the introduction it will be seen that k_0 and ΔE of the several feldspars can be calculated from these curves. And although the curves are approximate and idealized, and although much more chemical and mineralogical data are necessary for an exact treatment it may be stimulating for those who prefer an algebraic for a geometrical interpretation to give here the preliminary computations rather than await additional experimental and analytical information. With these reservations the figures of the following table 2 should be studied. k_0, and

Table 1.

POTASH FELDSPARS (AFTER HEIER, 1960).

K, Na in per cent, other elements in p.p.m.

Nos.	Li	Na	K	Rb	Ba	Sr	Cu	Pb
293	8.7	1.81	10.59	350	10000	1200	1.3	10.9
251	9.0	1.71	10.29	370	10000	1300	8.5	9.9
238	6.0	1.94	10.34	737	2500	650	15.5	11.4
224	4.7	1.54	10.99	532	10000	1400	0.7	11.4
An 12	5.5	1.26	11.42	475	10000	1600	8.2	9.6
25	4.3	1.51	11.37	700	6000	1000	2.4	21.1
47	6.4	1.13	11.82	518	8000	850	3.7	14.1
An 1	tr	0.80	12.48	306	4300	540	0.6	20.5
1 a	0.76	2.71	9.55	344				4.4
1 b	0.66	1.07	11.83	450				3.4
2	1.00	1.97	10.13	280				1.9
3	—	1.14	11.54	760				2.6
4	0.8	1.82	10.58	825				12.0

PLAGIOCLASES (AFTER HEIER, 1960).

Nos.	Li	Na	K	Rb	Ba	Sr	Cu	Pb
293	17.6	5.52	1.16	24	388	671	15.4	26
251	11.7	6.14	0.71	10	219	666	21.5	21
238	13.5	5.03	0.53	19	542	640	98.0	32
225	2.8	5.90	0.54	15.3	308	828	7.7	25
An 12	17.5	5.25	1.39	31.5	830	945	9.2	40
25	10.9	5.44	1.32	45	967	770	24.0	37
37	2.8	6.05	0.93	27	686	926	4.1	26
An 1	9.1	6.08	0.80	49	452	601	48.6	52
1 a = 1 d	1.6	7.57	0.58	18				6.5
1 b = 1 c	1.7	6.53	2.99	110				10
2	5.8	6.38	0.83	1.5				105
3	4.7	7.57	0.79	40				20
4	6.1	7.76	0.23	41				26

POTASH FELDSPARS (AFTER HOWIE, 1955).

Nos.	Li	Na	K	Rb	Ba	Sr	Cu	Pb
2270	tr	1.12	12.1		5000	1000		—
137	—	—	11.5		3000	1000		45
6436	3	1.38	11.1		1750	250		20

PLAGIOCLASES (AFTER HOWIE, 1955).

Nos.	Li	Na	K	Rb	Ba	Sr	Cu	Pb
2270	6	5.1	0.92		250	1700		10
137	—	5.2	—		125	800		30
6436	20.7	5.6	0.28		30	250		30

ΔE have been computed from fig. 2. H is the energy of formation of Na, Ca, Sr, Ba feldspars from the oxides estimated by SCHIEBOLD (1931) and by RAMBERG (1953). ΔE and H are in calories per mole.

Table 2.

$\ln k_o$	$k_o = \dfrac{x_1}{x_2}$	ΔE	H (1931)	H (1953)
Na 2.0	7	5400	59000	—
Ca 2.0	7	6500	61000	59000
Sr 5.7	300	8200	92000	78000
Ba 9.2	10000	10000	133000	93000

Most authors have contended that Ba concentrates in alkali feldspar, Sr in plagioclase. Now it is seen that the sorting of these elements between alkali feldspar and plagioclase depends upon temperature: at temperatures in the range of crystallization of igneous rocks, Ba strongly prefers alkali feldspar (the coefficient of distribution being around 100), and so does Sr, although to a less degree. At lower temperatures, however, this relation is reversed. Below ca. 450° C. for Sr, and below ca. 250° C. for Ba, plagioclase is preferred as the host mineral. Thus coexisting orthoclase and plagioclase crystallized from hydrothermal veins (in the range 200–300° C.) would take about equal amounts of Ba, whereas the amounts of Sr would be about ten times as high in plagioclase as in orthoclase.

It is premature to discuss the reasons for Ba and Sr preferring the alkali feldspar lattice at elevated
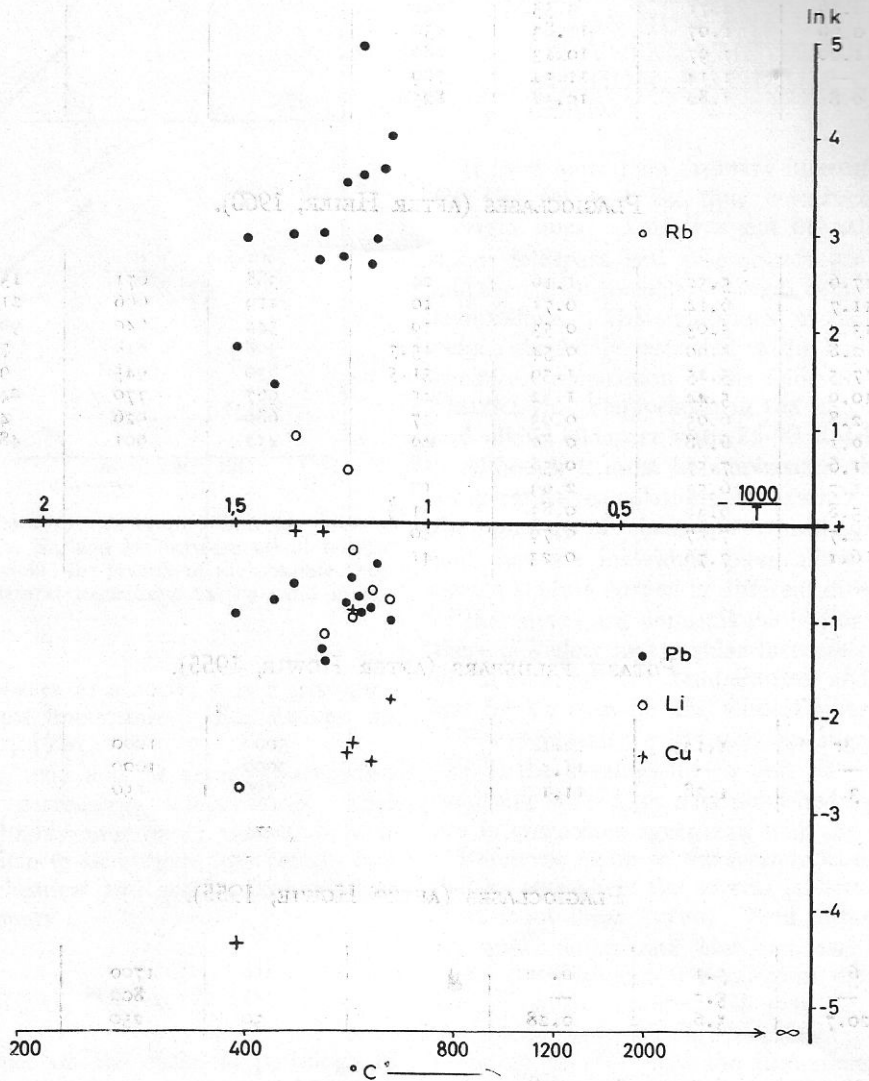

Fig. 3.—Individual values for the ratio of distribution of Li, Rb, Pb, and Cu between alkali feldspar and plagioclase plotted against temperature. Axes as in fig. 2.

temperature and the plagioclase lattice at low temperatures. The following suggestions are offered: The ions of Ba and Sr are closer to K than to Ca in size, but chemically they are more similar to Ca. May be that the size relations become more important at higher temperatures, while the similarity in chemical bonds is more important at lower temperatures. Again the simultaneous substitution of Si by Al may take place more readily at high temperature. DONNAY and DONNAY (1952) have called *effective radius* the radius increased by thermal motion. The rate of increase with temperature is different for different ions, consequently the size relations also change with temperature, a fact which will affect the ratio of distribution.

In fig. 3. are plotted the ratios of distribution of Li, Rb, Cu, and Pb against temperature. It is clear that Rb prefers alkali feldspar, whereas Li, Cu, and Pb prefer plagioclase (*). But otherwise the plots are scattered quite unsystematically over the area of projection.

Why should there be this difference in the behavior of Sr and Ba on the one hand and Li, Rb, Cu, Pb on the other?

Barium and strontium enter the feldspar lattices in rather large amounts; in terms, of feldspar molecules the order of magnitude is around one per cent. The other trace elements are present in much smaller amounts. In several interesting papers DEVORE has indicated that a trace element will not be accepted in regular lattice sites until its concentration is large enough to control the environment of this site. To explain the presence of small amounts of an element in a mineral DEVORE (1955) postulates a special kind of adsorption and surface reaction mechanism: Anions associated with cations of the trace element in the disperse phase develop bonds to one of the main elements near the surface of the mineral. Thus the trace elements are fixed in positions outside the regular lattice sites, they do not replace a main element of similar size but are simply present as imperfections in the crystal structure. DEVORE's analyses indicate

that trace elements with large ionic potentials will adhere to major elements with small ionic potentials, and vice versa.

Although this kind of sorting is no apparent in fig. 3, the fact that the minor trace elements are unsystematically distributed between the feldspar phases, whereas Sr and Ba, which both are present in rather large amounts, are regularly distributed, supports the main idea of DEVORE.

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(*) Lack of data makes it impossible to postulate any general rule; for there exist very few determinations of the trace elements in coexisting feldspars.

DISCUSSION

(see also the discussion to the paper by WINKLER)

SCHERMERHORN (Maquela do Zombo, Angola):

1. In many granites metasomatic alterations may have changed the composition of the feldspars. — For instance, a high-temperature K-Na-feldspar may have become homogeneous microcline while the oligoclase may have been decalcified to albite. In that case the k ratio would indicate a temperature of formation that would be too low as most or all sodium would have entered the plagioclase.

2. In other rocks the existence of zoned feldspars renders difficult the use of the k ratio as a geological thermometer.

YODER (Washington):

The new experimental data on the feldspars at various pressures indicate that the compositions of coexisting feldspars are dependent on pressure as well as temperature. Will it not be necessary to specify the pressure before use can be made of the compositions of coexisting feldspars as a geologic thermometer?

BARTH (Oslo), correspondence:

I have repeatedly affirmed that the two-feldspar geologic

thermometer is affected by pressure, as are all other geological thermometers known to me. Indeed, temperature, pressure and bulk composition of the rock are all important factors, but neither is susceptible to a rigorous mathematical treatment. Therefore an «average» empirical curve relating temperature with the compositions of coexisting feldspars in *granites and gneisses* has been constructed. It is believed that the variation in pressure or in composition from one such rock to another will not seriously affect the position of this curve.

On coexisting feldspars and their temperature of crystallization

by HELMUT G. F. WINKLER.

Marburg/Lahn (Germany), Mineralogisches Institut der Universität.

ABSTRACT

Coexisting feldspars have been formed during experimental metamorphism of rocks. The ratio of Ab in alkali feldspar to Ab in plagioclase (k-value) is discussed in relation to (a) temperature of formation and (b) chemical composition of the polycomponent rock system.

Observations on the solvus relations of alkali feldspars in experimentally metamorphosed rocks are dealt with.

A geologic thermometer has been proposed by TOM F. W. BARTH (1956) on the basis of the k-ratio, i.e. the ratio of distribution of the mol fraction of ab in alkali feldspar to the mol fraction of ab in plagioclase. This ratio is determined from the compositions of alkalifeldspar and coexisting plagioclase in a rock. BARTH has drawn a curve which gives the direct relation between the k-ratios and the feldspar crystallization temperatures and he says that this curve gives temperature indications to ± 50° C.

In the course of experiments on the metamorphism of rocks we had the possibility to test this feldspar geologic thermometer. I should like to describe briefly the results obtained in two different approaches, which all took place under 2000 bars of H_2O-pressure and in sealed gold containers:

(1) The k-ratios have been determined in experimentally formed metamorphic mineral assemblages which had been sujected to different temperatures. The chemical composition and the pressure remained in each case the same, while only the temperatures varied.

(2) The k-ratios determined at the same temperature and pressure but with chemically slightly different metamorphites have been compared, whereby the influence of the chemical composition can be demonstrated.

My co-worker H. STEUHL (1960) has made an experimental study of the metamorphism and anatexis of a paragneiss from the Black Forest: The rock, consisting of quartz, oligoclase, alkalifeldspar and biotite, has been powdered and isochemically subjected to different temperatures under p H_2O of 2000 bar; each run lasted for 3-4 weeks, after which equilibrium has been obtained. In these experiments metamorphic reactions took place by which —among others— the amount of alkalifeldspar increased above 600° C. while the amounts of biotite and plagioclase decreased, and some titanite was formed. At 675° C. the formation of an anatectic melt begins which a.

700° C. has dissolved all the alkalifeldspar together with the cotectic amount of quartz. Therefore plagioclase with coexisting alkalifeldspar are present up to that temperature only.

The composition of the plagioclase and the coexisting X-ray perthitic alkali-feldspar have been determined at different temperatures between 550° and 690° C. From the refractive index n_Y the total composition of the cryptoperthite was obtained according to TUTTLE (1952); accuracy ± 5 % Ab. In addition, in two cases (samples 670° and 690°) the alkalifeldspars have been seperated and homogenised and the position of the (201)-line gave compositions very close to those of the optical determination. The plagiocla-

Table I.

COEXISTING FELDSPARS.

°C	Cryptoperthite total composition		Plogioclase		k-ratio
	weight % Ab	mol % Ab	weight % Ab	mol % Ab	
gneiss	25	26	71	72	0,36
550	25	26	71	72	0,36
580	25	26	71	72	0,36
600	29	30	71	72	0,42
620	34	35	71—72	72	0,49
640	42	43	71	72	0,60
660	49	50	73—71	74—72	0,68— 0,70
670-680	Formation of partial melt begins				
680	50	51	73—70	74—72	0,69— 0,71
690	50	51	73—70	74—71	0,69—0,72
700	all alkali feldspar dissolved in anatectic melt				

ses are according to the Γ value of SMITH and GAY (1958) intermediate in thermal state, but with rising

temperature they approach more and more the high-temperature state, which is reached near 840° C. The composition of the plagioclases have been determined from the n_X value with the graph by J. R. SMITH (1958) up to 650° and above that temperature with the graph by SCHWARZMANN (1956), in TRÖGER (1956). Table I summarizes the compositions of the feldspars, which coexist in the metamorphic rock at different temperatures; the resulting k-ratios are given in the last column.

We note a change of the k-ratio with increasing temperature, but it is not an even change. This is
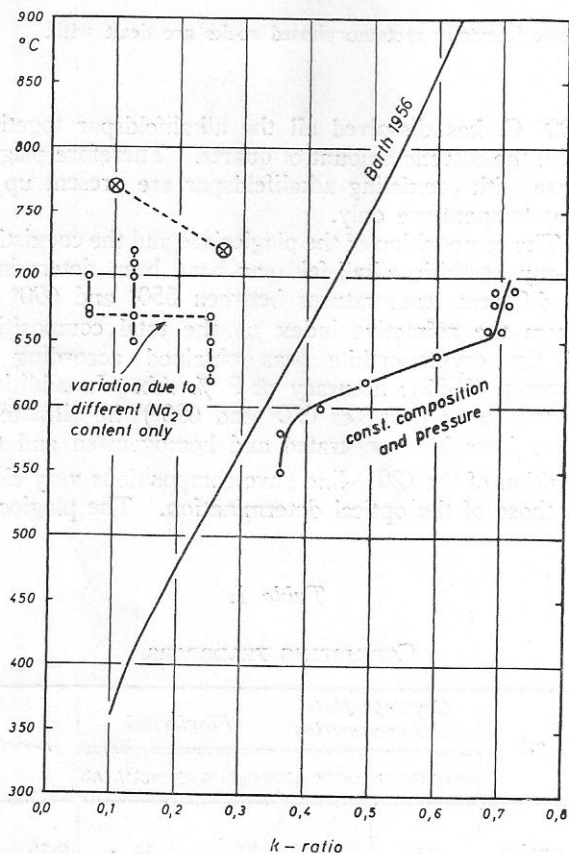

Fig. 1.—Ratio of mol-% Ab in alkalifeldspar to mol-% Ab in plagioclase versus temperature of crystallization of the coexisting feldspars. Data from various experiments and their relation to the curve proposed by BARTH (1956).

fully realized, if the k-ratios are plotted against temperature in fig. 1 (right hand side). The variation of k with temperature in the range from 580° to 660° is much more pronounced than that given by the BARTH-curve, while below 580° C. and above 650° C. it is much less. No part of our curve coincides with that given by BARTH. Although the chemical composition of the gneiss and the pressure remained constant, the variation of the distribution-coefficient with temperature can obviously be much more complicated than it would be if the distribution-law would be valid.

From the diagram we note that in the range from 660° to 690° C. and from 550° to 580° C. there is no or hardly any change of the k-ratio with temperature. This effect is observed over an even wider temperature range of up to 70° in other experiments, which already have been published (WINKLER u. v. PLATEN, 1958).

Starting from illitic clays, cordierite-bearing mineral associations of quartz, plagioclase and coexisting alkali-feldspar with only traces of biotite and sometimes sillimanite formed by mineral reactions above 625° and 600° C. respectively during the experimental metamorphism under constant H_2O-pressure of 2000 bar. The chemical compositions of these metamorphites were different only in regard to Na_2O; the proportions of all the other oxides were unaltered, because only Na had been added in different amounts to the same illitic clay which had been subjected to metamorphism. The compositions of the alkali-feldspars, which in all these cases were homogenous and contained only up to 18 % Ab, have been determined by X-ray methods. The compositions of the plagioclases could only be determined indirectly, from the knowledge of the bulk chemical composition and from the facts that all the Ca is located in the An-component of the plagioclase and that Na is only contained in the determined amounts of the alkali-feldspar and in the Ab-component of the coexisting plagioclase, the amount of which has also been determined. The compositions of the coexisting feldspars are summarized in Table II.

It should be noted that equilibrium had been established in all these experiments, for the results are the same wether obtained by heating up or by cooling down from the anatectic melt.

Table II

ALBITE-COMPONENT IN COEXISTING FELDSPARS OF HIGH GRADE METAMORPHITES, DERIVED FROM AN ILLITIC CLAY WITHOUT AND WITH ADDITION OF Na.

Ab-component		k-ratio	temperature	Na_2O weight % (mol %)
weight % resp. (mol %) alkali feldspar	plagioclase			
2,5±1 (2,5)	41 (42)	0,06 ± 0,02	670, 675, 700	0,43 (0,42)
8,5±1,5(8,5)	67 (68)	0,13±0,02	650, 670, 700 710, 720	1,36 (1,32)
18 ±1 (19)	74 (75)	0,25±0,02	620, 630, 650 670	2,11 (2,07)

It is noted from Table II that in each of the three cases the k-ratio does not show any variation over the investigated temperature-range; i.e. it remains unchanged over the temperature range of at least 30°, 70° and 50° respectively. This observation is also

presented in fig 1 (left side). Here again, as in the case previously dealt with, we have temperature ranges where the k-ratio of a given rock-composition does not change at all.

On the other hand, the k-ratios of the feldspars in the three different mineral-associations are distinctly different, having values of 0,06; 0,13 and 0,25 respectively. This is not due to different temperatures of crystallization but solely to the difference in chemical bulk composition of the three rock-systems. As stated previously, it is the content of Na_2O only, which is different in the three systems. If we plot the three k-ratios for 670° C. and 2000 bar of H_2O-pressure (which each remains unchanged at higher and/or lower temperature) against the mol-% of Na_2O which is present in the respective metamorphic rock (last column of Tab. II), we arrive at an aproximatively linear relationship (see fig. 4 in WINKLER und v. PLATEN, 1958. p. 102). It thus has become obvious, that the bulk chemical composition influences very greatly the k-ratio, i.e. the composition of coexisting feldspars. It should be noted, that this is the case, although the chemical differences are not exceptional but are all within the range of para-cordierite-gneisses.

From this last observation one would expect that with increasing Na_2O-content the k-ratio would generally increase also. This is certainly not always the case; other chemical components are also of influence: Consider the above mentioned rock, which contains 2 % Na_2O and 1,3 % CaO and has a k-ratio of 0,25, and add to it CaO in the form of 5 or 8 % of calcite, then no alkalifeldspar at all is formed during metamorphism, but only pure potassium-feldspar and An-rich plagioclase coexist in the highest metamorphic facies (ca. 700° C.), besides quartz, biotite and 5 % or no cordierite, respectively. The addition of CaO shifts the k-ratio from 0,25 to zero!

If then the Na_2O-content of these Ca-enriched rocks is increased from 2 to 3 %, the additional Na does not distribute itself among the *two* feldspars but only the plagioclase increases its Ab-content while the K-feldspar does not take up any Na (WINKLER u. v. PLATEN, 1960). Here, increase in Na-content has no longer any influence on the composition of the alkalifeldspar. In fact, the presence of the higher amount of CaO makes the k-ratio zero, despite a high amount of Na_2O.

With the addition of 8 % $CaCO_3$ to our Na-enriched illite-quartz clay a para-biotite-gneis without cordierite is produced under high-grade metamorphism; the k-ratio in this rock is zero. On the other hand the para-biotite gneiss from the Black-Forest, which has been dealt with at the beginning, exhibited at 690° C. a high k-ratio of about 0,7. These two metamorphic mineral-assemblages are qualitatively the same in so far as they represent biotite-plagioclase-alkalifeldspar-quartz-associations; but chemically, and therefore quantitatively, and concerning the compositions of the

plagioclase and the alkali-feldspar, they differ from each other, as do the k-ratios.

As shown in Table III, the main chemical differences of the rock (2) with the high k-ratio compared with the other one (1) are a smaller amount of CaO and Al_2O_3 and a higher amount of SiO_2 and FeO. The higher amount of SiO_2 is reflected by a higher conten of quartz, and that of FeO by a higher content of biotite, which has the consequence of less K-feldspar acting as a component in the alkalifeldspar. The smaller amount of CaO and Al_2O is reflected in less anorthite, being a component in the plagioclase (An 29); this, in turn, leaves SiO_2 uncombined, which thus increases the amount of quartz. The amount of the albite-component in the two rocks is the same due to the same amount of Na_2O. All this is well understood, by why does the Ab-content distribute itself in such a strikingly different way, giving a k-ratio of 0,7 in one case and of zero in the other case of para-piotite-gneiss? The explanation is not

Table III.

CHEMICAL AND MINERALOGICAL COMPOSTIONS OF TWO PARA-BIOTITE-GNEISSES MADE BY EXPERIMENTAL METAMORPHISM, (WEIGHT-%).

	1	2		1	2
SiO_2	57,9	64,4	quartz	19	30
Al_2O_2	20,0	15,3	biotite	11	20
Fe_3O_3	3,4	2,8	k-feldspar-component	12	5,5
FeO	1,0	3,0	albite-component	30	30
MgO	2,4	2,1	anorthite-component	27	9
CaO	5,7	2,8	compositon of alkalifeldspar	Or 100	Or 50
Na_2O	3,6	3,6	composition of plagioclase	An 47	An 29
K_2O	3,0	2,7			
miscell.	3,0	3,3	k-ratio	0,0 at 690°	0,7 at 690°C

1 Metamorphite at 690° C. and 2000 at H_2O-pressure, from illitic-quartz-clay with addition of 8 % $CaCO_3$ and 6 % NaCl.
2 Para-biotite-plagioclase-gneiss from the Black-Forest, Germany, treated at 690° and 2000 at H_2O-pressure.

known and is not simply given by the higher Na_2O : CaO ratio. This shows that —besides temperature and, probably to a lesser extent, pressure— chemical factors govern in a rather complicated manner the distribution of Na among plagioclase and coexisting alkalifeldspar in a rock system.

It must be noted here, that BARTH himself was fully aware of the influence of the chemical bulk composition on the distribution of sodium, and he felt that different curves of temperature versus k-ratio may be drawn for different bulk compositions as the effect of the chemical composition becomes better unders-

tood. But we are far from understanding the complex interrelations of the different variables.

This is, once more, illustrated, if one takes also into consideration the pairs of feldspars which coexist together with liquid and gas in the system An-Ab-Or-H_2O. YODER and collaborators (1957) have determined the composition of the plagioclase and alkalifeldspar coexisting at 720° and 770° C., respectively, and at 5000 bars. From their data a k-ratio of 0,27 is derived for 720° and of 0,10 for 770° C. These have also been plotted in fig. 1; encircled crosses. It is seen that the position of these points in the graph are unrelated to the other points· and although they show a temperature-dependence, this is just contrary to the direction which one should have supposed and which is given by the BARTH-curve. I feel that the compositions of coexisting feldspars should be investigated whenever this is possible but that their compositions can at present not give any indications of their temperature of crystallization.

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DISCUSSION

(see alto the discussion to the paper by BARTH)

BARTH (Oslo):

The work of professor WINKLER is a graphical demonstration of the complexities of the feldspar problems, the difficulties in the experimental approach, and the uncertainties in the application of the data. We do know that in many synthetic products, and also in the mineral assemblages of many natural rocks, there is a lack of equilibrium. In the treatment of such rocks the tools of physical chemistry are hard to use. But we also know that during the formation of many rocks there has been a remarkable approach to equilibrium; this applies likewise to metamorphic rocks, and to rocks containing two feldspar phases.

If x_1 and x_2 are the concentrations of sodium in coexisting alkali feldspar and in plagioclase respectively, T temperature, and P pressure, there can be no doubt that the following relation holds:

$$f(x_1, x_2, T, P,) = O$$

In my paper of 1956 on the two-feldspar geologic thermometer I have shown that *within a limited* range of composition the relation approaches:

$$\Phi(x_1/x_2, T, P) = O$$

This equation evaluated in its first approximation neglecting variations in pressure is the two-feldspar geologic thermometer proposed by me.

It should always be used with great care. Excerpt loc. cit. p. 13: «It can be seen graphically that ... Δ E depends on the composition, and the distribution law of van 't Hoff and NERNST is not ... valid .... Composition, both indirectly by inducing structural inversions, and directly, influences the distribution of soda, and the feldspar geologic thermometer ... should be adjusted for different compositions of the feldspar phases».

This thermometer seems to give reasonable and consistent values for many crystalline schists, gneisses, and granites. But it may be useless for certain other types of rock; lavas, for instance, which have been fumed and altered by vapors, as were the synthetic products of professor WINKLER, give unreliable and erratic results. But this does not detract from the value of the thermometer in other connections.

It is quite clear that the quantitative composition of the two feldspar phases in a rock is an important parameter that may shed new light on the genetic relations. It is important, therefore, that in all petrographic work, not only the composition of the plagioclases but also the composition of the alkali feldspars is quantitatively determined. Only in this way is it possible to obtain the exactness and sharpness of definition required by modern petrology, only in this way can one determine the temperature of formation, or of recrystallization of a rock.

WINKLER (Marburg). Answer:

1. Equilibrium has been demonstrated, especially well in

the most important experiments, which show the influence of the Na-content on the k-ratio at the *same* temperature.

2. I agree that the k-ratio of lavas means nothing in this connection, because they have not reached equilibrium and may even later be altered by vapors. But I cannot see, why this should apply to the feldspars of my experiments, for the vapor is in equilibrium with the solid phases.

3. It was the aim of my paper to convey this meaning, that the two-feldspar geologic thermometer as proposed by professor BARTH «should always be used with great care».

4. I fully agree, that the quantitative composition of the two feldspar phases should be determined in all petrographic work. It is very meritorious of professor BARTH to have pointed out that this may be genetically important.

HAFNER (Zürich):

The difference between your k-value measured at 500-600° C. and the one expected by Prof. T. F. W. BARTH could be explained by the assumption that orthoclase goes into solution while sanidine crystalizes. The k-value of partly ordered orthoclase might be different from that of completely disordered sanidine.

PREISINGER (Wien):

I would like to add the following remarks to the problem of co-existing feldspars: H. G. F. WINKLER's k-values refer only to feldspars which are not in equilibrium with liquid and gas whereas H. S. YODER refers with the term «co-existing feldspars» to those that are in equilibrium with li-quid and gas.

J. V. SMITH (Chicago). Question to PREISINGER:

There is great interest in the applicability of the distribution ratio proposed by Prof. BARTH. Have you taken the experimental data of YODER, STEWART and J. R. SMITH and calculated the distribution ratios, and if so do they agree with the values proposed by BARTH for natural feldspars?

PREISINGER (Wien). Answer to SMITH:

If you put in the experimental values of H. S. YODER, you get quite different values of the distribution ratio.

Comments on the «Two-feldspar geothermometer» and K-feldspar obliquity (*)

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INTRODUCTION

It has been requested that I comment on the "two-feldspar geothermometer". This note consists of such comments plus some additional remarks concerning my current investigation which amounts to an evaluation of the possible uses of K-feldspar obliquity determinations as a petrogenic tool.

It seems only prudent to preface these remarks by noting that they must be considered to be those of a petrologist!

THE TWO-FELDSPAR GEOTHERMOMETER

This section consists of a summary of a previously published discussion (DIETRICH, 1960) plus certain elaboration and a brief presentation of subsequently discovered, pertinent relationships.

The two-feldspar geothermometer suggested by BARTH (1934) and used chiefly by him and some of his students (e.g., BARTH, 1956 and HEIER, 1960) plus other distribution-between-feldspar geothermometers such as those discussed by BARTH at this symposium have great appeal because of their being based on these common rock-forming minerals. But, numerous contingencies render their validities questionable (see especially BARTH, 1951, p. 148-151 and 1956, p. 12-14 and DIETRICH, 1960, p. 41-53). Especially noteworthy are the following:

1) temperature values have been fixed on the basis of unproved empirical data;
2) the total amount of sodium in the system may affect its distribution in the phases;
3) pressure which, as well as temperature, controls the distribution is not taken into account;
4) some two-feldspar rocks may not be susceptible to two-feldspar geothermometer analyses;
5) one of the commonly employed methods tends to yield material with too low Ab:Or ratios

for the "average" K-feldspar of many rocks; and
6) at best, only the most recent lowest temperature at which equilibrium existed between the feldspar phases is recorded.

To consider these aspects in the listed order:

1) The fact that this geothermometer has not been found, to the present, to be susceptible to laboratory checking accounts for its being based on empirical data (some of which may need modification—see 5). Perhaps future laboratory investigations or, as suggested by MACKENZIE at this symposium, crosschecking betwen this method and a method involving the structural state of the plagioclase and/or K-feldspar will aid to eliminate this difficulty.

2) That the total amount of sodium in the system may affect its distribution in the two feldspar phases has been suggested on the basis of theoretical considerations by BARTH (1956, pp. 12-14) and as an implication of experimental work by WINKLER and VON PLATEN (1958, pp. 99-102). Both appear mainly to suggest that so far as this is concerned the geothermometer should be restrcted to determination of relative temperatures within comparatively small zones and that rocks with relatively low ($<$ 2.0 per cent) or high ($>$ 6.5 per cent) Na$_2$O-contents should be delimited from such considerations.

Along this line, there are other aspects that also need investigation both singly and in combination to ascertain their individual and interdependent effects —for examples, the possible effects of: a) the presence of one versus other types of K-feldspar, i.e., as to structural state and possibly even as to perthitic variants— especially their possible control over process(es) and completeness of sodium distribution between and within diverse phases during metamorphism; b) the presence of one versus other composition plagioclase feldspars, including zoned versus unzoned ones; c) the grain sizes of the rocks d) the presence versus absence and, if present, the composition of volatiles; and e) the types of aggregation of the rocks of which they are constituents.

3) Possible effects of pressure on distribution of elements among diverse solvents in systems are known incompletely. Perhaps, in the case of two-feldspar

geothermometer application to individual rocks, pressure effects are essentially negligible —because of the states in which equilibria are probably established and because of the rather restricted volumes involved. Nonetheless, past and present day interpretations must be considered "pressure dependent".

4) Some of the reasons why certain two-feldspar rocks may not be susceptible to two-feldspar geothermometric analyses are mentioned in a preceding paragraph concerned with sodium distribution factors. The geneses of perthites and zoned plagioclases and their implications so far as interpretations of geothermometers involving them are also of extreme importance. For example, if the potassium feldspar is perthitic, to be useable the perthitic quality must have originated as the result of either exsolution or simultaneous crystallization of the phases from an originally homogeneous alkali feldspar but not as the result of replacement. The worst part of such contingencies as these is that most decisions as to which rocks are and which are not susceptible to use are strictly subjective.

5) One of the methods commonly used to separate the K-feldspar from the rock consists of grinding the rock until complete liberation is effected and then fractionating the ground material on the basis of specific gravities (using liquids) until a "final" fraction is collected, checked optically, and found to be "pure" K-feldspar. Such separation usually results, in my opinion, in analyses of a K-feldspar fraction with an Ab:Or ratio lower than the average for the whole grains of the checked specimen for two reasons: a) grinding for liberation results in breaking of the original grains so that individual pieces have different Ab:Or ratios unless the original whole grains are homogeneous (commonly a single grain in a phanerite will be broken into more than 200 pieces with Ab:Or ratios probably ranging from 1:0 to 0:1) and, b) once so divided, the material can be separated into an almost infinite number of "pure" K-feldspar fractions with their specific gravities varying directly with their Ab:Or ratios. (This has been proved to take place!) Thus, if only a "last" fraction is used, it is almost bound to have an Ab-content which is less than the average Ab-content for the original whole grains. Mrs. B. NILSSEN of the Mineralogisk Museum of Oslo has been working on this and suggests that heating before final grinding to liberation may be a way to overcome this —perhaps she will add a few words on this. To me, however, this brings up an even more basic question— what if the unequal distribution is of a zoned nature?

Such zoned alkali feldspars have been reported *(e.g.,* SCHERMERHORN, 1956 and DIETRICH, 1961). These reported ones, however, would have led to no difficulties so long as intensive petrographic studies were made — the inhomogeneities were microscopically visible and the rock would not have been subjected to such analyses. But, what of inhomogeneities not microscopically visible? (If relationships similar to those reported by SCHERMERHORN and by DIETRICH were present submicroscopically, analyses of carefully "picked" material might even indicate that the central portions of the K-feldspars were formed at relatively lower temperatures than their marginal portions!)

6) Undoubtedly for those who do employ this geothermometer in any way, the fact that is of utmost importance is that for many rocks the true significance of the temperature obtained cannot be much more than guessed unless the thermal history of the rock is known. This is true because *the most recent lowest temperature at which equilibrium existed between the feldspar phases is necessarily what must be recorded*. This, of course, means that even if it is assumed (even if correctly so) that the present contents of the feldspars do reflect simultaneous crystallization from a magma or former established equilibrium conditions, the temperature which obtained at the time of last attainment of these conditions —and, thus, the temperatures "measured"— could have been much lower than the highest temperature to which the rock material was exposed (see Fig. 1). This diagram is reproduced from my 1960 paper in which the curves are discussed. Suffice it to repeat here that so far as this aspect is concerned: a. probably the thermometer is best for rocks formed as the result of relatively rapid cooling of a magma— the temperature recorded would be essentially that of consolidation; b. contrariwise, probably the most completely misleading temperatures that may be obtained will be those for exposurewise geologically isolated, non- to slightly-metamorphosed, quartz-cemented arkosic sedimentites that consist chiefly of granule-sized, monmineralic fragments derived from a relatively rapidly cooled magmatic rock; and, c. whereas a magmatic temperature can be cited as fairly acceptable evidence for a magmatic origin, a submagmatic temperature cannot be cited as evidence against an ultimate magmatic origin.

All of the aspects mentioned here need further investigation! Until numerous points are clarifield, I believe that it is best to use these geothermometers with the full realization that they have their true value essentially restricted to determination of relative temperatures of certain composition rocks with essentially equal grain sizes within comparatively small zones.

K-FELDSPAR OBLIQUITY

Since the work of MACKENZIE (1957) on the structural state of the Na-feldspars and especially that of GOLDSMITH and LAVES (1954 & 1954a) on the structural state of the K-feldspars, a number of workers have determined the obliquity (or "triclinicity") of
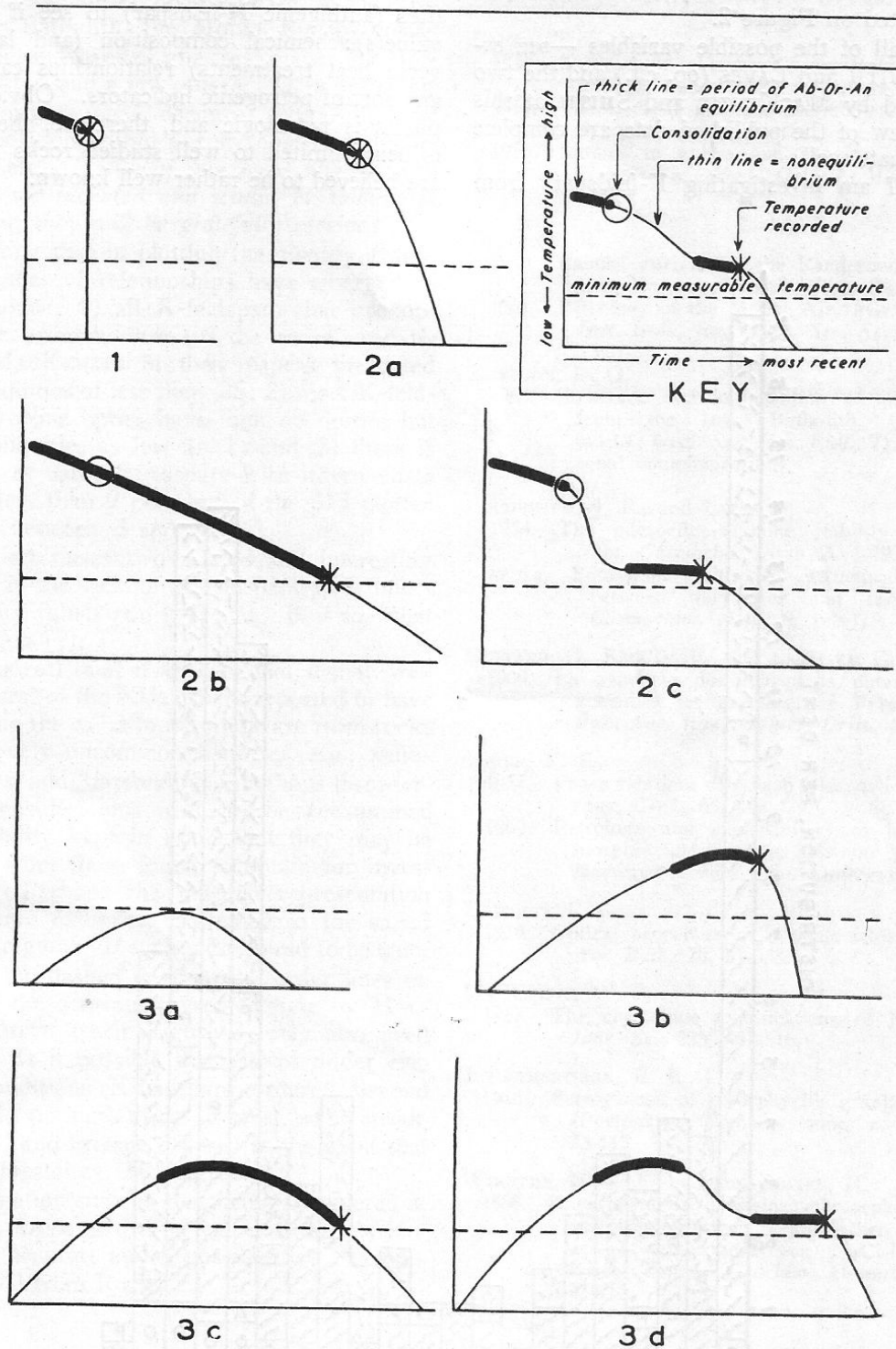
Fig. 1.—Generalized possible thermal history curves for: 1. extruded or intruded-into-«cold»-rocks magma, 2a. intruded-into-«cool»-rocks magma, 2b. very slowly cooled magma, 2c. erratically slowly cooled magma, 3a. low grade metamorphism, 3b. higher grade metamorphism with slow cooling during waning stages, 3c. higher grade metamorphism with very slow cooling during waning stages, 3d. higher grade metamorphism with erratic cooling-even diaphthoresis-in post-highest temperature metamorphism period.

natural K-feldspars from numerous types of rocks. Most of those published and many which are unpublished are plotted on Figure 2.

Considering all of the possible variables —see especially GOLDSMITH and LAVES (op. cit.) and the two papers presented by MACKENZIE and SMITH at this symposium— few of the published data are complete enough to evaluate well.

At present, I am investigating K-feldspars from certain volcanics, plutonic masses and series, pegmatites, diverse grade metamorphic rocks, and sedimentites (authigenic K-feldspar) to see if any obliquity value(s): chemical composition (and later these: diverse heat treatments) relationships can be used as any sort of petrogenic indicators. Obviously, the emphasis is petrologic and, therefore, the investigation is being limited to well studied rocks whose origins are believed to be rather well known.
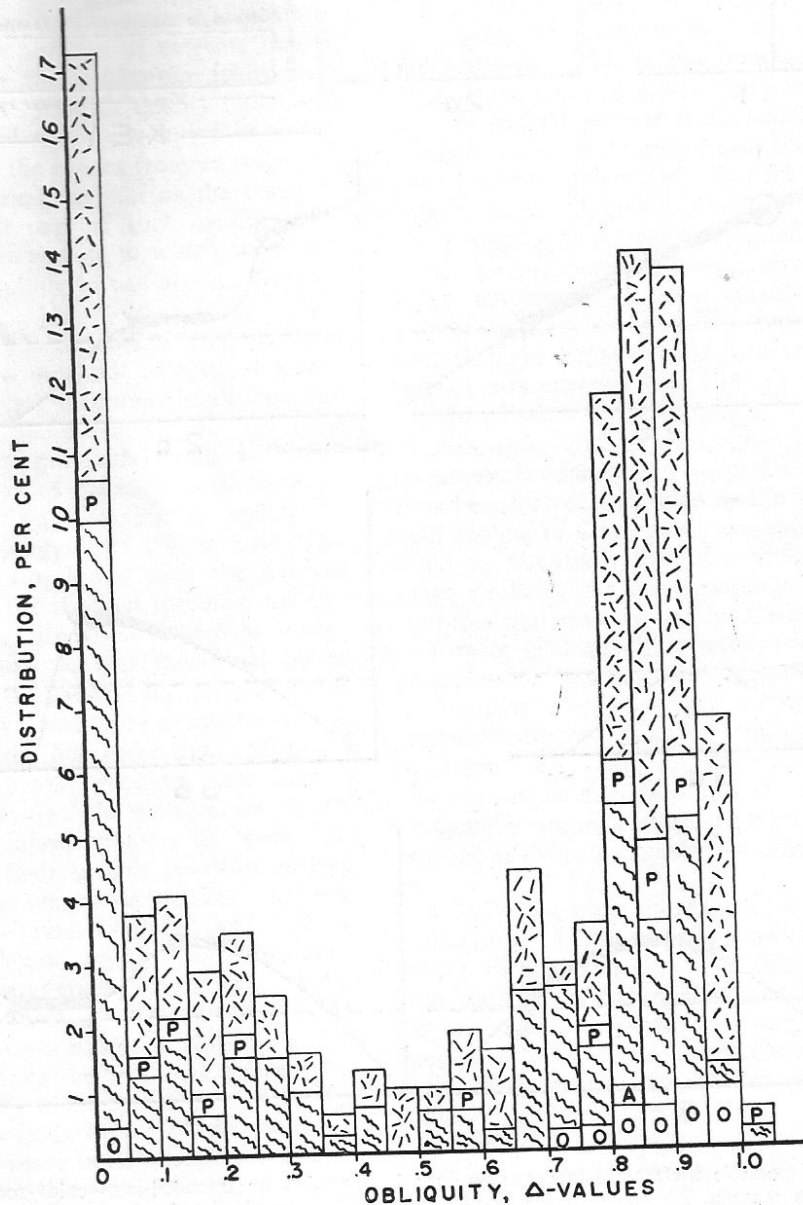
Fig. 2.—Distribution of Obliquity values (Δ) for 315 K-feldspars. Considering the *x*-ray setups and measuring techniques used, it appears likely that some of the values reported as «0» (and, therefore, plotted as 0-.05) may actually have Δ-values of up to .25. Legend: irregularly spaced and oriented lines-plutonic rocks, P-pegmatite, wavy lines-metamorphic rocks, A-authigenic K-spar, and O-others. Data from EMERSON (1960), GOLDSMITH and LAVES (1954 & 1954a), GUITARD *et al.* (1960), HEIER (1957 & 1960), HEWLETT (1959), and unpublished data of the writer.

Already included are rocks from the various phases of the Oslo Plutonic Series, diverse phases of the composite Boulder Bathylith, the Mount Rogers volcanics, the Randesund banded gneisses, numerous Norwegian pegmatites, and a few others. Data are being plotted as to origins, ages, chemical compositions of the feldspar, position within porphyroblasts and phenocrysts, etc., etc. *If any of you have samples you would like to see included and would be willing to contribute them, they will be gratefully received.*

It is interesting that in plotting the already available data a number of relationships have emerged as possibly obtaining: 1) all K-feldspars that are optically sanidine or orthoclase (in the sense used by SMITH and MACKENZIE in their papers presented here) have obliquities of less than .25; 2) most K-feldspar with microcline optics have high obliquities but a few have obliquities as low as .1; and, 3) there is a marked lack of natural feldspars with intermediate obliquities — less than 9 per cent of the 315 plotted have Δ- values between .3 and .65.

The last aspect raises two related and interesting questions: a. is the lack of K-feldspars with intermediate obliquity values real (?); and, b. if so, what is the explanation (?).

If the lack is real (and it appears that it may well be because several of the K-feldspars reported to have obliquities within the ca. .3 to .65 range are from rocks with comparatively uncommon histories, *e.g.*, xenoliths, porphyries, and "farsundite"), perhaps disorder-temperature considerations need to be reëxamined with the possibility kept in mind that they may be quite different from those found to obtain for investigated alloys. Perhaps the graphic representation would be a curve exhibiting flattening in the ca. .3 to .65 Δ-value region. If such were found to be true, the spacing of the dashed degree-of-disorder lines on the Or side of the diagram presented here by MACKENZIE and SMITH (their Figure 3) may also need to be revised. Is it possible that except under certain special conditions K-feldspars ordered beyond where they yield Δ-values of ca. .3 must, so to speak, "jump the gap" and become ordered to the point that they yield Δ-values of ca. .60 or greater?

Before information such as that being considered at this symposium becomes of real value to the petrologist, it must be accurate and if possible tied to empirical data derived from Rocks.

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DISCUSSION

LAVES (Zurich):

Professor DIETRICH's collection of Δ-values of K-feldspars (rather randomly taken) and its use for plotting a curve: frequency versus Δ (fig. 2) is of highest interest. Some comments may be permitted:

1. Professor DIETRICH states that he used the words sanidine and orthoclase «in the sense used by SMITH and MACKENZIE in their papers presented» at this symposium. He could have said equally well: in the sense of LAVES and GOLDSMITH in the paper presented at this symposium. Namely, as long as optical symmetry is concerned there is no difference of opinion between the viewpoints of S. and M.

on the one side and L. and G. on the other side. The differences emerge if it comes to the problem of the structural meaning of the word «orthoclase» and its phase-relation-implications.

2. With respect to the sentence just before Professor DIETRICH's observations suport very well the viewpoints of GOLDSMITH and LAVES: He finds «orthoclases» with obliquities up to 0.25 and «microclines» with obliquities down to 0.10. This indicates that he found some orthoclases which have *structurally* a higher obliquity than some of the K-feldspars which he classified as microcline for optical reasons.

3. Professor DIETRICH raises two questions: (a) is the relatively rare occurrence of K-feldspars with intermediate obliquity values real?; and (b), if so, what is the explanation?

As to (a) the writer is convinced that it is real. As to an explanation of (b) the following suggestions may be presented (see also the writers discussion of the paper by MACKENZIE and SMITH, this symposium, especially his points C, E and F, pages 66 and 67).

α) Regardless of growth temperature most K-feldspars grow (disordered enough) as a virtually monoclinic phase (called by us sanidine).

β) At temperatures below the transformation temperature monoclinic → triclinic (still unknown but estimated to lie near 500° C) Al-Si ordering sets in to such a degree that triclinic domains are formed («left» and «right» ones with equal probability, due to the monoclinic ancestry). As long as these domains are too small to be recognized optically and as long as they do not yield X-ray diagrams which would allow the assignment of an obliquity value we call such material «orthoclase». (Thus, it may well be that a material appears *optically* as an «orthoclase», but *to X-rays* as a microcline; see point 2 above.)

γ) Within the «orthoclase»-state the triclinic domains may lack of sharp boundaries, i.e. an over-all structure coherency may well prevail for a considerable amount of time and counteract (as the consequence of stress-strain relations) the development of increasing Al-Si order, say higher than one corresponding to $\Delta \approx 0.2$.

δ) A next step in reaching the state of equilibrium will be a cosiderable loss of structure coherency, i.e. incoherent domain boundaries are formed. After the coherency restrictions for further ordering have thus vanished the ordering process proceeds with a speed that is (among others) a function of the difference between the degree of order present and the equilibrium degree of order. If the equilibrium conditions to be reached require high order (high obliquity) the stages of intermediate order (intermediate obliquity) will be passed with a relatively high speed and they are, therefore, relatively rare in nature. — These suggestions are rather well illustrated by the observations presented by Karamata (this volume, p. 127-130).

4. Considering the above suggestions and the very low speed of the ordering process *at* low temperatures the present writer does not see right now that it be necessary to «reëxamine» the «disorder-temperature considerations» hitherto developed, at least not as far as the principles are concerned. He still believes in the strong analogies between the order-disorder (substitutional) behaviour of alloys and feldspars, except that many alloy systems investigated untill now and published on responded to temperature changes during laboratory times rather well whereas the K-feldspars are very reluctant to do so. They need, apparently, geological times for approaching the equilibrium state of such low temperatures at which microcline of high obliquity is the stable modification. (Experiments under pressures exceeding those of natural conditions may help in speeding up the ordering process to such a degree that the kinetics of it may be studied eventually).

Lower temperature terminations of the three-phase region plagioclase-alkalifeldspar-liquid

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ABSTRACT (*)

Experimental and geological evidence indicates that in the system Or-Ab-An the three-phase field, plagioclase-alkali feldspars-liquid, terminates in several different ways under different conditions. The likely terminations have been developed from Schreinemaker's rules governing the disappearance of three-phase fields. Some terminations are transitional into each other as the conditions of crystallization change.

In nature the important variables are the relative amounts of additional components, total pressure, and feldspar phase transitions.

It may be possible to identify the type of termination involved in the crystallization of some rocks. The necessary data are the amounts and compositions of both kinds of coexisting feldspar and of the feldspar components of the coexisting liquid at one or more stages of the crystallization process. Mantling of alkali feldspar by plagioclase and vice versa can be explained by some terminations. With all of the types of termination, extensive fractionation yields a liquid rich in Or and Ab.

DISCUSSION.

Rosenqvist (Oslo):

Do you regard the considerations given as also valid for triclinic K-feldspars with decreasing temperature?

Roseboom (Washington). Answer:

We have considered the symmetry of the feldspars to be that of the high temperature forms because these appear to be common in natural and synthetic magma. Change of feldspar symmetry may be accompanied by change in feldspar composition, and the phase relations will of course be changed, but the direction and amount of such changes are not well known at present.

Stewart (Washington). Answer to Yoder:
The question was not received:

It should also be noted that the effect of additional components on the temperature of the liquidus is similar to that of higher H_2O pressure, so that it may be difficult to separate these effects in the field

Study of extrusive rocks rich in Ab will indeed be especially informative about the position of the critical point on the solvus, and we await the results eagerly.

(*) Reprinted from the program, distributed in Copenhagen, August 1960, as no manuscript was received.

Echange des atomes dans les feldspaths. Action de l'eau

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RÉSUMÉ

Par l'étude des différentes phases solides que l'on obtient dans l'échange des cations dans les feldspaths alcalins et dans les plagioclases, soit par voie hydrothermale, soit par voie sèche à température élevée au contact de sels fondus, on essaie d'interpréter le mécanisme de l'action de l'eau.

On met en évidence que la mobilité des ions alcalins, quand l'eau est présente, entraîne celle des ions Si et Al; et les formes basse et haute température des feldspaths alcalins se différencient bien par l'arrangement des ions Si et Al.

Il est bien connu que la synthèse des feldspaths alcalins et des feldspaths calco-sodiques est très facile dans un large domaine de température dès que l'eau agit sous pression.

Dans ces conditions hydrothermales, nous avons montré (Wyart, Sabatier, 1956-a) qu'au dessus de 400° et à des pressions d'eau de quelques centaines de bars, les feldspaths donnent lieu à des échanges d'ions et se comportent, à ce point de vue, comme des zéolites.

MOBILITÉ DES ATOMES DANS LES FELDSPATHS ALCALINS

Par exemple, en présence d'une solution de Na Cl à 10 g. par litre, la sanidine, en poudre fine, est complètement transformée en analbite en 24 heures à 500° C. sous une pression de 650 bars.

Dans ces réactions, le rôle de l'eau apparait d'une manière éclatante. si l'on considére les transformations mutuelles des feldspaths alcalins (Wyart, Sabatier, 1956-b).

Ainsi, l'albite (*) et l'analbite chauffées en présence d'une solution de chlorure de potassium, entre 400 et 700° C., sont transformées complètement en K AlSi$_3$O$_8$, et le diagramme de poudre du produit obtenu est celui de la sanidine. Mais il n'en est pas de même si, au lieu de se placer dans des conditions hydrothermales, on opère par voie séche.

En chauffant l'albite (forme B. T.), à 600°, dans le mélange eutectique de fluorure et de bromure de potassium ou bien à 900° dans le chlorure de potassium fondu, on obtient la forme basse température du feldspath potassique, le microcline, comme l'avait déjà obtenu Laves à 1060° C. (1951, p. 511-2). En

partant de l'analbite on aboutit, dans ces conditions, à la sanidine.

De même, entre 400° et 700°, en présence de solutions de chlorure de sodium, on transforme la sanidine ou le microcline en analbite; tandis que, par voie sèche, soit à 680° avec le mélange eutectique bromure et fluorure de sodium, ou à 900° avec la chlorure de sodium fondu, on obtient l'analbite si on part de la sanidine, l'albite si on part du microcline.

Tableau I.

REACTIONS D'ECHANGE D'IONS DES FELDSPATHS ALCALINS.

Température	Au contact des sels fondus
600°C et 900°C	Albite + K ⟶ Microcline + Na
600°C et 900°C	Analbite + K ⟶ Sanidine + Na
680°C et 900°C	Microcline + Na ⟶ Albite + K
680°C et 900°C	Sanidine + Na ⟶ Analbite + K

Température	En présence d'eau
400°C à 700°C	Albite + K ⟶ Sanidine + Na
	Analbite + K ⟶ Sanidine + Na
	Microcline + Na ⟶ Analbite + K
	Sanidine + Na ⟶ Analbite + K

Ces résultats, groupés dans le tableau I, s'expliquent clairement si l'on admet qu'un même squelette aluminosilicique AlSi$_3$O$_8$ que nous avons désigné "trame B. T.", est présent dans le microcline et l'al-

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(*) Dans la suite de cet exposé, nous désignerons sous les noms d'albite et d'analbite les formes basse (B. T.) et haute-temperature (H. T.) de NaAlSi$_3$O$_8$ et sous les noms de microcline et de sanidine les formes basse et haute-temperature de KAlSi$_3$O$_8$.

bite, formes de basse température, et qu'un même squelette AlSi$_3$O$_8$, dit "trame H. T.", est présent dans l'analbite et la sanidine, formes de haute température.

Par voie sèche la trame, c'est-à-dire l'arrangement des ions Al, Si, O, se conserve quand les ions alcalins s'échangent; au contraire, en présence d'eau, il n'en est plus de même, car dans tous les cas, on obtient la trame H. T.

Ces résultats soulignent bien l'action profonde de l'eau; dès que celle-ci est présente, même à une température aussi basse que 400° on obtient toujours, après échange des ions Na$^+$ et K$^+$, les formes réputées stables à haute température; au contraire, par voie sèche, on peut obtenir, à température élevée, 900°, et même 1060° dans l'expérience de LAVES concernant le microcline, les formes basse température que sont l'albite et le microcline.

Il est intéressant de confronter ces résultats avec l'hypothèse d'un arrangement différent des Al et des Si dans les formes haute et basse température, et avec les structures atomiques fournies par TAYLOR et BAILEY (1955); FERGUSON, TRAILL et TAYLOR (1958). Dans les formes H. T. sanidine et analbite, les Si et les Al se remplaceraient d'une manière désordonnée, tandis que leur arrangement serait ordonné dans les formes B. T. que sont l'albite et le microcline. Il faut alors, dans le cadre de cette hypothèse, admettre que, même à une température aussi basse que 400° C., l'eau pénètre dans le milieu cristallin, en même temps que les ions Na$^+$ ou K$^+$, c'est ce que nous voulons maintenant démontrer.

MOBILITÉ DES ATOMES DANS UN PLAGIOCLASE

Nous avons utilisé un plagioclase dont la composition chimique répond à la formule K$_{0.02}$ Na$_{0.39}$ Ca$_{0.59}$ (Al, Si)$_4$O$_8$; c'est celle d'un labrador; nous avons utilisé ce labrador, soit réduit en poudre de 20 microns, soit sous forme de cristaux uniques pour réaliser les expériences suivantes.

a) *Action de KCl fondu sur la poudre.*

La poudre placée dans K Cl fondu, à 900° C., donne lieu à un phénomène d'échange de Na$^+$ et de K$^+$, la teneur en calcium n'est pas modifiée car un ion Ca^{2+} ne peut être remplacé par deux ions K$^+$. La vitesse de diffusion est lente, mais au bout de cent heures, on obtient une phase solide homogène de composition: K$_{0.28}$Na$_{0.13}$Ca$_{0.59}$ (Al, Si)$_4$O$_8$.

Le cliché de poudre (fig. 1 b), voisin de celui du labrador initial (fig. 1 a), caractérise un plagioclase, riche en potassium, que l'on ne trouve pas dans la nature. Ce n'est pas un minéral.

b) *Action d'une solution de KCl sur la poudre.*

Avec la même poudre, chauffée en autoclave, en présence d'une solution de KCl à 20 gr./lit., à 500° C. sous une pression de 600 bars, l'échange des ions K$^+$ et Na$^+$ est beaucoup plus rapide, l'analyse chimique montre qu'il est total au bout de 24 heures et la poudre a une composition chimique répondant à la formule: K$_{0.41}$Ca$_{0.59}$ (Al, Si)$_4$O$_8$.
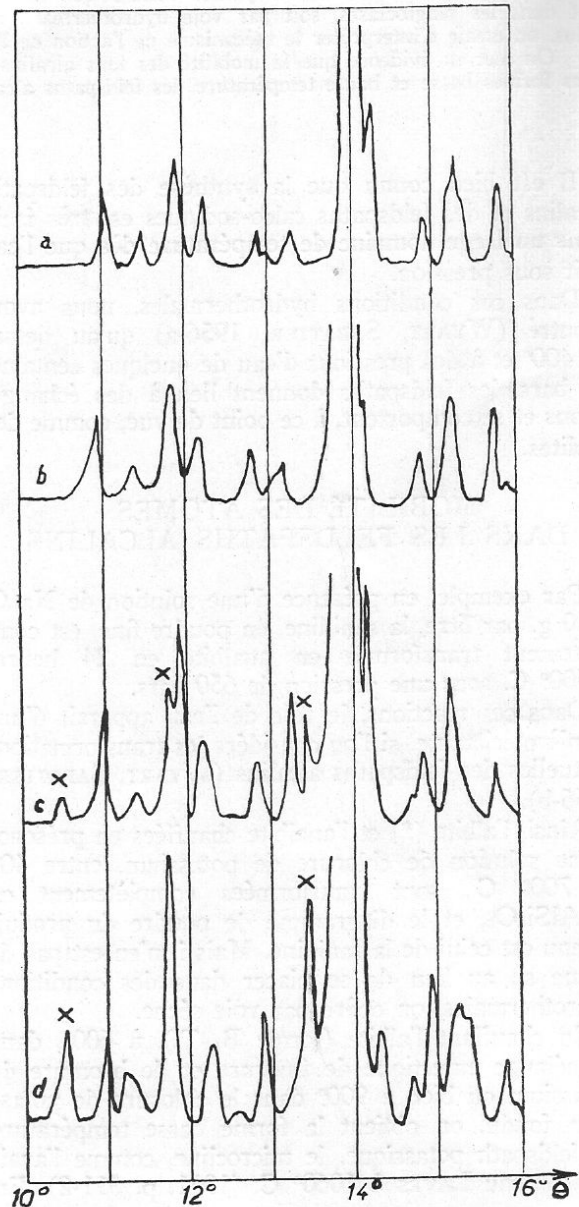
Les rayons X montrent qu'elle est constituée par

Fig. 1.—Diffractogramme entre 10 et 16° de l'angle θ de Bragg (rayonnement KαCu) du labrador: a) naturel; b) après traitement dans KCl fondu; c) après traitement dans KCl fondu, puis dans l'eau à 500°C; d) après traitement par une solution de KCl à 500°C. Les raies de la sanidine sont marquées d'une croix.

deux phases solides (fig. 1 d); l'une est la sanidine, l'autre un plagioclase voisin de l'anorthite.

Deux mécanismes peuvent être envisagés, pour expliquer cette réaction.

1) Au contact de la solution, chaque grain se dissout et recristallise en donnant les deux phases sanidine et anorthite.

2) La réaction s'effectue sans destruction de la phase solide; la diffusion des ions Na+ et K+ s'accompagne d'une diffusion des Si et des Al, de sorte que dans les régions riches en potassium on ait une "trame" AlSi$_3$O$_8$ et que dans les régions riches en Ca, prédomine la trame Al$_2$Si$_2$O$_8$.

Il est facile de montrer que c'est ce second mécanisme qui a lieu grâce à l'expérience qui suit.

placent dans le réseau cristallin en même temps que se produit l'échange des ions Na+ et K+.

Mais ce mouvement des Si et des Al peut se produire sans échange des ions alcalins, comme le montre clairement l'expérience suivante.

d) *Action de l'eau pure sur le "labrador potassique".*

Le feldspath en poudre obtenu dans l'expérience (a) qui est homogène, avec la composition K$_{0.28}$Na$_{0.13}$Ca$_{0.59}$ (Al, Si)$_4$O$_8$ est chauffé, à 500° C., dans un autoclave avec de l'eau *pure* sous une pression de 600 bars, pendant 24 heures.

On constate, avec les rayons X, la séparation en
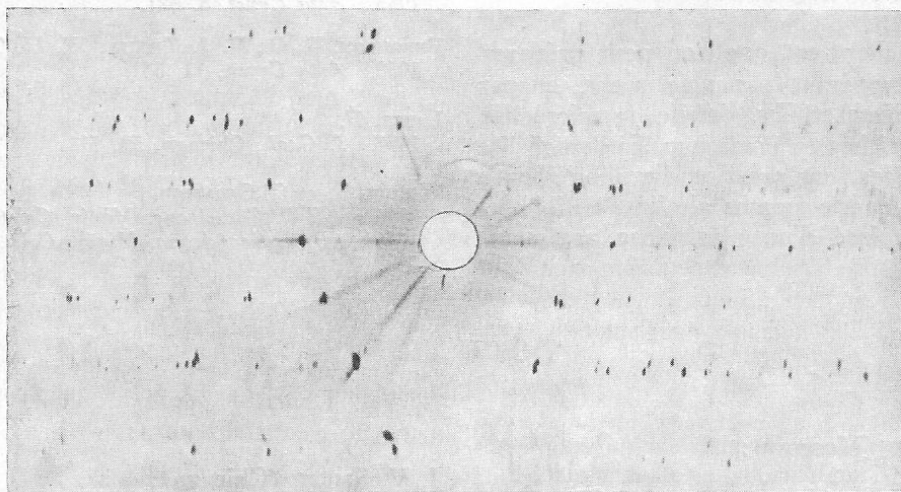
Fig. 2.—Diffractogramme de cristal tournant du labrador autour de [100] après traitement par une solution de KCl à 500° (K$_\alpha$Cu).

c) *Action d'une solution de KCl sur un monocristal de labrador.*

On a opéré avec la même solution, toujours à 500° C., sous une pression de 600 bars, sur des cristaux de quelques dixièmes de millimètre, limités par les clivages (001) et (010), assez petits pour que l'échange des ions Na+ par les ions K+ soit total au bout d'un temps assez court (72 heures) et assez grands pour effectuer avec eux des diagrammes de cristal tournant. Les cristaux ont conservé la même forme et les clichés obtenus en faisant osciller le cristal autour de la rangée [100] révèlent deux systèmes de strates parallèles (fig. 2). Le cristal est donc hétérogène et il est constitué de deux feldspaths, orientés l'un par rapport à l'autre, avec en commun la rangée [100]; pour l'un le paramètre *a* a pour valeur 8,61 KX, c'est celui de la sanidine, pour l'autre *a* = 8,20 KX, il caractérise l'anorthite.

Dans cette expérience les ions Si^{4+} et Al^{3+} se dé-

deux phases, l'une sanidine, l'autre plagioclase riche en anorthite (fig. 1 c).

En résumé, on peut provoquer un déplacement des ions Si^{4+} et Al^{3+} dans le réseau cristallin du labrador, à 500° C. sous quelques centaines de bars de pression d'eau. D'autres expériences effectuées à 600° ont donné le même résultat. Par contre à 900°, mais à sec nous n'avons pu mettre en évidence une mobilité de ce genre.

A 500° ou 600° C., le mouvement des Si et Al est considérablement accéléré par la présence de l'eau sous pression. A ces températures, et en l'absence d'eau, aucun déplacement des Si et Al n'a pu en effet être mis en évidence.

e) *Chauffage à sec du "labrador potassique".*

Ainsi, le "labrador potassique" homogène de composition K$_{0.28}$Na$_{0.13}$Ca$_{0.59}$ (Al, Si)$_4$O$_8$ chauffé une se-

maine à la pression atmosphérique à 500° ou 600° reste homogène.

Il en est de même si on le chauffe 72 heures à 600° sous une pression de 560 bars d'azote. Nous avons vu que dans ces conditions, mais en remplaçant l'azote par l'eau, les raies de la sanidine apparaissent au bout de 24 heures, témoignant du déplacement des Si et Al.

Il est difficile de concevoir que l'eau puisse accélérer ces transformations sans pénétrer dans le réseau cristallin. Pourtant elle n'y laisse aucune trace car l'analyse chimique montre que le produit final des réactions, contient moins de 0,1 % d'eau (le dosage étant effectué sur le produit séché à l'air). L'article suivant suggère par quel mécanisme l'eau pourrait intervenir.

CONCLUSION

Ces expériences montrent que l'on peut préparer au laboratoire, en opérant par voie sèche, et par échange des ions Na+ et K+, l'albite, le microcline et des plagioclases riches en potassium. Si l'on réalise les mêmes expériences sous pression d'eau, on aboutit aux formes H. T. des feldspaths alcalins, analbite et sanidine, et à la place d'un plagioclase potassique homogène en obtient un mélange de sanidine et d'anorthite.

L'analyse de cette dernière réaction montre qu'elle résulte d'une diffusion des ions Si^{4+} et Al^{3+} à l'état solide, et qu'à des températures de 500 et 600° cette diffusion ne se produit qu'én présence d'eau sous pression. Ceci suggère que dans les réactions d'échanges sous pression d'eau, qui conduisent des feldspaths alcalins B. T. aux formes H. T., l'eau agit sur la "trame" $AlSi_3O_8$ de ces minéraux, et que ces formes B. T. et H. T. diffèrent par l'arrangement des atomes Si et Al, ce qui est en bon accord avec les déterminations structurales.

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DISCUSSION

D. S. KORZHINSKY (Moscow):

As geological evidence shows, in metamorphic processes water may percolate through feldspar crystals playing a decisive role in the transformation of feldspars, in agreement with Prof. WYARTS considerations. As I tried to show in my paper of 1940 (Liquid inclusions as the cause of imaginary pelitization of feldspars. Comptes Rendus (Doklady) de l'Acad. de l'URRS. V. XXIX N2) dusty feldspars, erroneously described as «pelitic» or «pelitized» have mostly no pelitic particles, but are overfilled with minute fluid inclusions, sometimes smaller than 0,5 micron in diameter. Such dusty feldspars, especially orthoclases, are formed when they grow unstable and therefore more soluble, but the conditions are unfavorable for their complete transformation to a stable form.

WYART (Paris). Answer:

Cette observation du Prof. KORZHINSKY confirme l'importance de l'eau dans la genèse des feldspaths.

J. V. SMITH (Chicago):

Fudali, a student of Prof. TUTTLE at Pennsylvania State University, has heated feldspars in alkali chloride solutions in hydrothermal bombs. Single crystal X-ray studies showed partial conversion to a sodalite-type phase. Has Prof. WYART observed sodalite in his work?

WYART (Paris). Answer:

Nous n'avons jamais observé la formation de sodalite au cours de nos expériences; ces dernières ont été répétées par P. M. ORVILLE au Geophysical Laboratory of the Carnegie Intitution of Washington (Annual report of the director of the Geophysical Laboratory, 1958-1959, p. 118-121) qui ne parait pas non plus avoir observé la formation de ce minéral et qui retrouve, en les complétant, nos résultats.

Echanges isotopiques des atomes d'oxygène dans les silicates et mécanisme d'interaction eau-silicate

par J. WYART, H. CURIEN et G. SABATIER.
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RÉSUMÉ

L'échange isotopique d'oxygène entre des échantillons de silicates ou de granite et de l'eau fortement enrichie en ^{18}O a été étudié expérimentalement en autoclave dans un domaine de température de 360° C à 800° C et sous une pression allant de 150 à 1800 bar. Dans le cas le plus défavorable (quartz à 360°, 170 bar), l'échange atteint un taux de 10 % en 24 heures. La fusion de l'échantillon facilite considérablement l'échange. Les résultats de ces experiences s'interprèten aisément dans l'hypothèse d'un mécanisme de réaction de l'eau sur les tectosilicates dans lequel les ions H^+ et H^- viennent rompre les liaisons Si-O-Si et Al-O-SI.

1. Introduction.

L'influence de l'eau sur le comportement thermodynamique des silicates, et des feldspaths en particulier, a été mise en évidence par de nombreuses expériences : le point de fusion du quartz et des feldspaths peut être considérablement abaissé par l'intervention d'une forte pression de vapeur d'eau, les verres peuvent être recristallisés et les transformations polymorphiques des feldspaths réalisées à des températures anormalement basses.

Il serait intéressant de connaître le mécanisme élémentaire qui, à l'échelle atomique, justifie l'intervention l'eau dans ces diverses modifications estructurales.

Dans ce but nous nous sommes proposés de suivre le comportement des atomes d'oxygène en réalisant les transformations structurales des silicates en présence d'eau fortement enrichie en ^{18}O. Une série d'expériences a déjà été réalisée (WYART et alt., 1959); d'autres sont en cours. Nous donnerons ci-dessous comme exemple les résultats obtenus dans deux types d'expériences simples : chauffage sans fusion, en présence d'eau, d'un minéral pur; fusion d'un granite sous pression de vapeur d'eau.

2.

Ces expériences sont réalisées dans des autoclaves du modèle décrit par J. WYART et G. SABATIER (1957). Après stabilisation, la température est maintenue constante pendant 24 heures. Après refroidissement, l'eau condensée peut être prélevée. Soit :

$$t_o = \frac{\text{nombre de noyaux d'}^{18}O}{\text{nombre total de noyaux d'oxygéne}}$$

le titre en ^{18}O de l'eau introduite dans l'autoclave, t son titre après l'opération. Les valeurs de t_o et t sont mesurées par spectrographie de masse au Service des Isotopes stables du Centre d'Etudes Nucléaires de Saclay [l'eau enrichie en ^{18}O a été également préparée dans ce Service]. La valeur t_i du titre initial en ^{18}O

du minéral est prise égale à 0.0020. Connaissant la composition du minéral et les masses d'eau et de minéral mises en présence, il est d'autre part immédiat de calculer t_e, titre d'équilibre auquel conduirait un équilibre isotopique parfait dans le système eau + minéral. La valeur du titre t de l'eau recueillie après l'opération doit donc être comprise entre t_o et t_e. L'importance de la réaction d'échange isotopique entre les deux constituants du système peut être représentée par la valeur du rapport

$$R = \frac{t_o - t}{t_o - t_e}$$

que nous appellerons taux d'échange. Ce taux serait nul s'il n'y avait pas d'échange; il vaudrait 1 si l'équilibre isotopique complet était réalisé.

3.

Echange isotopique de l'oxygène entre l'eau et une poudre de microcline à 690°. Le remplissage en eau de l'autoclave est calculé de façon à ce que la pression s'établisse à 400 bars. Les résultats obtenus sont indiqués dans le tableau I. On voit que, en 24 heu-

Tableau I.

Echantillon	$T\ °C$	Pression en bar	$t_o . 10^2$	$t . 10^2$	$t_e . 10^2$	R
Microcline	690	400	1.32	1.15	0.86	0.37
Granite (50 μ) { sans fusion	800	500	1.30	1.17	0.80	0.26
Granite (50 μ) { fusion	800	1800	1.41	1.04	0.89	0.72
Contrôle (sans silicate)	800	850	1.50	1.47		

R représente l'échange isotopique en 24 heures; t_o est le taux isotopique en ^{18}O de l'eau initiale, t le taux de l'eau après l'expérience, t_e le taux qu'on obtiendrait si l'échange avait été complet (équilibre isotopique).

res, le taux d'échange isotopique atteint la valeur 0,37. Une forte proportion des atomes d'oxygène dans la masse du silicate a donc été échangée, les liaisons Si-O-Si et Al-O-Si, en forte proportion, se sont donc temporairement brisées puis reformées. Pour évaluer l'effet des contaminations qu'auraient pu introduire les diverses manipulations subies par l'eau, nous avons réalisé un essai de contrôle, à 800°, avec un remplissage conduisant à une pression de 850 bars. On voit (tableau I) que la valeur t du titre final de l'eau (t = 1,47) diffère peu du titre initial (t_o = 1,50) et que les contaminations sont négligeables à la précision de nos expériences.
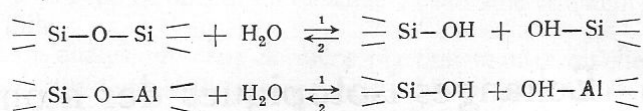
4. *Fusion d'un granite.*

Le granite utilisé est essentiellement constitué par du quartz, du feldspath alcalin et un peu d'amphibole sodique. Il est broyé en grains de 50 microns environ.

Dans une première expérience, le remplissage de l'autoclave est tel que, à 800° C., la pression s'établisse à 500 bars. Dans ces conditions, le granite ne fond pas. Le taux de l'échange isotopique ainsi obtenu en 24 heures est de 0,26, c'est-à-dire du même ordre de grandeur que dans l'expérience précédente sur le microcline (§ 3).

Dans une deuxième expérience, le remplissage de l'autoclave est calculé de manière à ce que, à 800° C., la pression s'établisse à 1800 bars. Dans ces conditions, le granite fond. On constate alors que le taux d'échange isotopique prend la valeur 0,72 (Tableau I). A température donnée et à durée égale, l'échange est donc considérablement augmenté du fait de la fusion. Les conditions physiques de contact entre les deux phases sont pourtant beaucoup moins favorables lorsque le granite est sous forme de masse fondue et non plus de grains très fins. On peut donc conclure que le mécanisme atomique de la fusion du granite sous pression de vapeur d'eau, à température anormalement basse, fait intervenir un échange effectif d'atomes d'oxygène entre le silicate et l'eau.

5.

Il est facile d'imaginer un tel mécanisme d'échange Celui qui paraît le plus vraisemblable peut être représenté par un schéma de réactions réversibles du type :

$$\equiv Si-O-Si \equiv + H_2O \underset{2}{\overset{1}{\rightleftarrows}} \equiv Si-OH + OH-Si \equiv$$

$$\equiv Si-O-Al \equiv + H_2O \underset{2}{\overset{1}{\rightleftarrows}} \equiv Si-OH + OH-Al \equiv$$

Dans le sens (2), l'élimination de l'eau se fait aux dépens de l'oxygène original du silicate ou de celui qui avait été apporté par l'eau dans le sens (1), ce qui constitue un mécanisme d'échange isotopique d'oxygène très efficace.

Dans le sens (1), les réactions conduisent à l'ouverture des tétraèdres structuraux, permettant ainsi les réarrangements ordre-désordre des ions Al et Si, provoquant la fusion à température anormalement basse, facilitant la recristallisation des verres.

Le mécanisme proposé attribue donc un rôle également important aux ions H+ et OH—. Le comportement des ions H+ pourrait être d'ailleurs indépendamment étudié par des méthodes isotopiques utilisant la radioactivité du tritium. La mise en oeuvre de ces méthodes est cependant plus délicate.

6.

Antérieurement à notre travail, des expériences d'échanges isotopiques dans les silicates avaient été réalisées par DONTZOVA (1956), qui avait étudié en particulier les échanges isotopiques avec CO_2 : dans ce cas, il nous semble probable que les échanges d'ions oxygène entre CO_2 et le silicate sont limités à la surface de contact, les atomes échangés pénétrant ensuite dans l'échantillon par diffusion. Des expériences récentes de WYLLIE et TUTTLE (1959) ont d'ailleurs montré qu'une forte pression de CO_2 *sec* n'abaisse pas (ou pratiquement pas) le point de fusion du granite et des feldspaths, et n'exerce aucune action favorable sur la cristallisation des verres.

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DISCUSSION

PREISINGER (Wien):

How large was the OH—-content in the crystals after the experiment and does this content depend upon pressure?

CURIEN (Paris). Answer:

Le contenu en eau des échantillons après les expériences est inférieur à 0,2 %. Nous n'avons pas de données sur sa variation en fonction de la pression.

ROSENQVIST (Oslo):

As the unmolten samples in your experiment are apparently unchanged, there may be a solution and redeposition from the gas phase. Independent of whether this mecha-

nism or the mechanism suggested by you, there is a problem of the diffusion rate and activation energy. Have you any indications as to the actual values of these parameters?

CURIEN (Paris). Answer:

Nous n'avons pas, jusqu'à maintenant, d'argument expé-rimental définitif pour éliminer l'hypothèse de l'échange par solution et redéposition, suivies de diffusion dans l'échantillon solide. Nous réalisons actuellement des expériences en vue de prouver la diffusion simultanée de l'hydrogène et de l'oxygène.

En vue d'obtenir des données quantitatives sur la cinétique nous nous proposons d'étudier l'échange dans des conditions physiques et géométriques bien définies, sur des monocristaux.

Les cavités des feldspaths

par Georges A. Deicha.
C. N. R. S. Faculté des Sciences, Sorbonne, Paris (*)

RÉSUMÉ

Répartition, morphologie et remplissage des lacunes de cristallisation des feldspaths, en rapport avec leur genèse.
Existence et signification des figures de corrosion naturelles dans les clivages des feldspaths constituants des roches.

Comme la plupart des minéraux les feldspaths ne sont que rarement exempts de lacunes de cristallisation. Pourtant, paradoxalement, même lorsqu'il s'agit d'exemplaires aussi faciles à étudier que les minéraux des trop classiques fentes alpines, la présence de ces cavités reste parfois systématiquement ignorée. Les descriptions par ailleurs minutieuses n'en font que rarement mention. Ainsi, j'ai eu l'occasion de le signaler l'année dernière à la suite de la conférence rapport de R. L. Parker lors de la réunion de l'I. M. A. à Zürich. Pour illustrer l'importance que peuvent prendre les lacunes de cristallisation dans de tels échantillons on peut prende pour exemple les "albites" du glacier de Tré-la-Tête (Val Montjoie, Massif du Mont Blanc, France). Le noyau initial de chaque cristal, où s'est en particulier effectuée l'amorce des macles et des groupements à axes parallèles, présente un aspect laiteux dû à l'abondance des inclusions aqueuses, alors que les régions marginales sont parfaitement limpides, et n'offrent, presque pas de lacunes de cristallisation. Le remplissage liquide de ces cavités permet d'observer des bulles de retrait correspondant à un degré de remplissage assez constant. De telles inclusions se prêtent parfaitement à des determinations thermométriques par la méthode de Sorby (Smith, 1954). Je pense que ceux qui s'intéressent à l'architecture des feldspaths alpidiques se devraient de considérer également la répartition, la morphologie et le remplissage de telles inclusions. J'estime en particulier que la récente étude de H. U. Bambauer et F. Laves, sur l'"adulaire" du Val Casaccia (Suisse) gagnerait à être complétée dans ce sens. J'ai d'ailleurs présenté une observation sur ce sujet lors de la derniére réunion de la Société allemande de Minéralogie à Wetzlar.

Des phénomènes cristallogénétiques comparables à ceux qui se sont produits lors de la croissance des albites et des adulaires hydrothermales sont également intervenus dans la genèse des feldspaths d'origine magmatique. Les beaux cristaux de "Sanidine" de la grande cascade du Mont-Dore (Massif Central français) me serviront d'exemple dans la présente communication. Comme il s'agit d'un matériel classique, il sera loisible pour chacun de développer mes quelques observations présentes. On sait que l'altération de la roche encaissante permet de dégager facilement ces phénocristaux, de la pâte, aussi est-on surpris de constater sous le microscope qu'ils recèlent encore des reliquats magmatiques vitreux. Les cavités contenant ces reliquats ne mesurent guère qu'une vingtaine de microns; le remplissage de celles qui sont plus grandes est géneralment dévitrifié.

Si c'est la fraîcheur du verre remplissant les lacunes de cristallisation qui attire de prime abord l'attention, celle-ci est ensuite fixée sur leur morphologie assez caractéristique: elles se présentent, sous un angle d'observation convenable, avec des contours grossièrement quadrangulaires. Les redents nombreux de ces contours se rapprochent de ceux des cristaux alpins dont il a été question plus haut. A première vue le contraste est assez marqué avec les reliquats magmatiques des quartz rhyolotiques (Deicha, 1955). Par contre la répartition et la fréquence sont assez semblables dans les deux cas; on constate en particulier l'abondance des reliquats magmatiques dans les fantômes d'accroissement. Le trouble qui caractérise ces derniers est dû, en partie, à la présence d'inclusions solides. Ces particules minérales étrangères sont presque toujours imparfaitement moulées par le feldspath hôte et il subsiste, au contact, des reliquats vitreux mineurs.

La disposition de ces reliquats mineurs est particulièrement spectaculaire sur les éléments cristallins aciculaires microscopiques: on observe de fines "gouttelettes" de verre fixées sur les aiguilles minérales qui les traversent parfois de part en part. Sur les éléments solides plus gros les reliquats vitreux occupent des positions souvent excentriques. En faisant ces observations on ne manque pas d'être frappé du fait qu'il existe généralement dans la sanidine des fissures liées à la présence d'inclusions. Ce sont les éléments cristallins étrangers les plus gros qui fournissent les plus grosses fissures. Il est tentant de les interpréter par des différences de coefficients de dilatation, voire par

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une éventuelle contraction brusque du feldspath hôte au cours du refroidissement. Cette dernière possibilité est encore étayée par le comportement des reliquats magmatiques vitreux : ceux-ci présentent tous une bulle très nette et relativement développée et pourtant presque tous sont auréolés par une fissure du minéral hôte. Ce phénomène est peut-être en relation avec des transformations structurales au sein du feldspath, on sait que la transformation $\alpha \rightarrow \beta$ du quartz donne lieu à des phénomènes semblades (BARRABÉ et DEICHA, 1956).

Dans la sanidine du Mont-Dore il existe, à côté des reliquats magmatiques primaires, des inclusions vitreuses secondaires. La relation entre ces deux types de cavités est souvent évidente : le magma des reliquats originels s'injectant partiellement dans les fissures y détermine des figures de corrosion, plus ou moins parfaitement isolées les unes des autres par des recristallisations. C'est d'ailleurs cette injection qui explique le développment insolite de la bulle dans la lacune de cristallisation maîtresse.

Si dans les deux exemples précédents les inclusions secondaires ne jouent qu'on rôle subordonné, il n'en est plus de même des feldspaths des roches plutoniques et métamorphiques. Dans les granites et les gneiss en particulier il n'est pas rare que le nombre de ces cavités doive se chiffrer en dizaines, voire en centaines de milliers au mm³. Leur présence avait été explicitement niée par certains pétrographes sur la foi d'études de lames minces ordinaires. Dans ces préparations microscopiques classiques il est en effet souvent vain de vouloir observer des cavités ayant gardé leur remplissage fluide originel ... alors que celui-ci est souvent inmédiatement trahi par le mouvement brownien de ses bulles, lorsque l'observation se

fait dans une esquille n'ayant subi aucun traitement thermique et un minimum d'actions mécaniques.

Faute de temps je ne m'attarderai pas sur ce dernier et plus important type d'inclusions. Pour autant cependant que l'étude des feldspaths doive servir à une meilleure connaissance de l'histoire naturelle des roches cristallines, il serait téméraire d'ignorer que bien souvent aucune portion de ces minéraux essentiels ne s'est trouvée à plus de quelques dizaines de microns de solutions aqueuses ayant imbibé la roche. Il serait vain de tirer des conclusions pétrogénétiques de la considération des structures cristallines en négligeant les observations microscopiques fines. Ces recherches aux forts grossissements constituent précisément le pont entre les techniques roentgenographiques et l'étude pétrographique telle qu'elle se pratique au microscope polarisant depuis un siècle.

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DISCUSSION.

WYART (Paris) :

Il serait intéressant de connaître la composition chimique des inclusions liquides dans les différents feldspaths. — Cela fournirait des renseignements précieux pour la compréhension de leur genèse. — A-t-on des renseignements précis à ce sujet?

DEICHA (Paris). Answer :

L'importante question posée par mon Maître, M. J. WYART me donne l'occasion de citer ici, en premier lieu la thèse fondamentale soutenue ici même à Copenhague, il y aura bientôt 20 ans, par un confrère danois, H. FABER (1941): «On the salt solutions in microscopic cavities in granite». *Danmarks geologiske Undersøgelse. II, Roekke 67.* A côté de cet ouvrage j'ai donné, a la suite de la communication No. 1 de la section 1 du présent Congrès géologique, une courte bibliographie. Parmi les recherches de plus en plus

nombreuses portant sur l'analyse chimique des fluides inclus, on peut distinguer deux groupes de travaux : ceux qui portent sur des quantités importantes de matière (parfois plusieurs kilogrammes) et ceux qui ne concernent que de petits groupes d'inclusions microscopiques, voire même des inclusions isolées. Ces dernières recherches offrent de grandes perspectives : ainsi la méthode simple pour l'identification et le dosage approximatif du CO_2 libre vient de faire l'objet d'une communication de J. RASUMNY au présent Congrès géologique ; cette communication a d'ailleurs été illustrée par la projection d'un film réalisé grâce à J. PAINLEVÉ. Il faut espérer que les moyens matériels mis à la disposition de telles études seront renforcés. Il suffira de lire les communications présentées au Congrès géologique en collaboration avec P. COLLOMB (section 14) et D. BOULANGER (section 17) pour voir la portée des résultats que des techniques microchimiques modernes pourraient fournir. A la suite de ces communications et de celles de mes confrères E. ROEDDER (section 16) et N. ERMAKOV (section 17), nous avons décidé la formation d'une association pour l'étude des inclusions fluides. Le developpement des méthodes d'analyse en est l'an des buts.

The structure of Orthoclase

by J. B. Jones and W. H. Taylor,
reported by H. D. Megaw.
Cavendish Laboratory, Cambridge, England.

ABSTRACT

A new structural study of orthoclase has confirmed that this feldspar shows a partially ordered Si, Al distribution. No final decision is reached on the true symmetry of orthoclase — whether monoclinic or an intimate intergrowth of triclinic units, but any departure from monoclinic symmetry is probably very small. The details of the structure are discussed in relation to those of sanidine and microcline, with special reference to the configuration of the tetrahedral groups, the environment of the potassium atom, and the application of the charge-balance hypothesis concerning the stability of the alkali feldspars.

This paper is an account of a redetermination of the structure of orthoclase by very careful two-dimensional work. The unfortunate clash of this meeting with the congress of the International Union of Crystallography in Cambridge has prevented Dr. Taylor from coming himself, and Dr. Jones is in Australia. Obviously I cannot speak with the same authority about the work, but I will do what I can.

The material is the same Spencer C which was previously studied by Chao, Hargreaves and

Taylor (1940). Photographs about the [100], [010], [001] and [$\bar{1}$10] axes were used (many of them taken by Prof. J. V. Smith). Intensities were measured visually; careful corrections were made for absorption and extinction. Refinement was done by Fourier methods, using difference maps. The final R-factor was 7.2 %.

Very careful attention was paid to the question of whether the symmetry might be truly triclinic, but no evidence for this was found, either in the cell dimen-

Table I.

(a) Interatomic distances in Å.

Si_1 —		Si_2 —		K —	
OA_1	1.651	OA_2	1.639	OA_1	2.898
OB	1.650	OB	1.624	OA_2	2.698
OC	1.654	OC	1.634	OB	3.029
OD	1.651	OD	1.633	OC	3.135
				OD	3.111
Mean	1.652	Mean	1.633		

	Tetrahedron 1	Tetrahedron 2
OA — OB	2.639	2.674
OA — OC	2.781	2.588
OA — OD	2.645	2.661
OB — OC	2.710	2.690
OB — OD	2.726	2.689
OC — OD	2.692	2.690

(b) Interatomic angles.

	Si_1	Si_2		
OA — Si — OB	106° 6′	110° 7′		
OA — Si — OC	114° 38′	104° 32′	Si_1 — OA_1 — Si_1	144° 12′
OA — Si — OD	106° 9′	108° 43′	Si_2 — OA_2 — Si_2	138° 50′
OB — Si — OC	110° 12′	111° 20′	Si_1 — OB — Si_2	153° 3′
OB — Si — OD	110° 0′	111° 9′	Si_1 — OC — Si_2	130° 54′
OC — Si — OD	108° 45′	110° 49′	Si_1 — OD — Si_2	141° 44′

3

very weak streaks, much weaker than the weakest intensities; they were ignored. There was no reason for handling the work with any other symmetry than the conventional space group $C2/m$.

The bond lengths and bond angles are given in Table I. Notice the difference in size between the two tetrahedra. It is important to know if it is real. Calculation of the standard deviation by the method of Lipson and Cochran, depending on the evaluation of the background over the whole area of the map, gave a value of 0.014 Å for the S. D. of a bond. This would not class the difference as significant. But there are several reasons for considering this unduly pessimistic. (1) Inclusion of the background close to the atoms tends to an overestimate. (2) In fact the difference between the tetrahedral means remained constant during refinement, while the scatter of individual values was decreasing. (3) Comparison of the structure, bond by bond, with sanidine shows all the details faithfully reproduced, including the irregularities of the tetrahedra. (4) Estimation of the S. D. from the scatter of bonds *within* the tetrahedra gives a much smaller value, about 0.0014 Å.

Hence it seems clear that the "Si₁" positions are more Al-rich than the "Si₂" positions. I come back to this point later.

The point about the irregularity of the tetrahedra is worth noting. It has generally been assumed that Si tetrahedra are regular or, if irregular, that the differences are small and random. But here are some very large differences. Notice in particular the bond OA-OC, where the difference is 0.2 Å. A similar difference is found in microcline, sanidine and even celsian, as shown in Table II. The effect in celsian (where one of the long edges is in a tetrahedron predominantly Si, the other predominantly Al) shows that

Table II.

	OA—OC BOND LENGTHS IN Å		
	IN		*Difference*
	tetrahedron 1	*tetrahedron 2*	
Orthoclase....	2.781	2.588	0.193
Microcline........ {	2.744	2.552	0.192
	2.834	2.577	0.257
Sanidine..........	2.743	2.600	0.143
Celsian { B₁ (O), B₁ (z)	2.786	2.638	0.148
{ B₂ (O), B₂ (z)	2.911	2.554	0.357

it does not depend on the Si/Al distribution, but must be due to the general balance of forces in the feldspar structure between the tetrahedral cation and O on the one hand, the large cation and O on the other.

The next point concerns the temperature factors (Table III). Those for Si/Al and O would not be

considered abnormal for a structure with site disorder; they are *exactly* the same as those for the average structure in celsian. But the K atom needs further consideration. It had an average temperature factor of 1.4, intermediate between sanidine and microcline, but difference maps showed that it was anisotropic, with the shortest axis along a^*. Re-examination of sanidine and microcline showed that there too the atom was anisotropic in the same way. The actual values of the anisotropy were not measured.

The peak heights at 'Si' differed for 'Si₁' and 'Si₂', which had values of 51.2 and 54.1 $eÅ^{-2}$ respectively, the difference being more than three times the S. D., which is 0.6 $eÅ^{-2}$. This difference was unexpectedly large. Again the data for sanidine and microcline were re-examined, and it was seen that in sanidine the difference is zero and in microcline it is like that in orthoclase, but not quite self-consistent, suggesting the need of further study before conclusions can be drawn.

Coming back to the very important question of Si/Al distribution, and using SMITH's end-values for

Table III.

"TEMPERATURE" FACTORS.

(I)   *Isotropic values of B* (Å²):

	Orthoclase	Microcline	Sanidine
K	1.4	1.0	1.9
Si/Al	0.6	[Bragg and West	]
O	1.2	curves used	

(II)   *Anisotropy of K in orthoclase:*
        $B_x = 1.0$ Å²   along a^*
        $B_y = 1.8$ along b
        $B_z = 1.5$ along c

Si and Al, we find for 'Si₁' and 'Si₂' contents of 0.30 Al and 0.19 Al respectively, as compared with the predictions of FERGUSON, TRAILL and TAYLOR (1959) of 0.36 Al, 0.14 Al for the material which they call 'ideal orthoclase', but which I should prefer to distinguish by some other name —perhaps 'optimum orthoclase'— keeping the adjective 'ideal' for what is ideal geometrically rather than electrostatically or thermodynamically. Geometrically ideal orthoclase would have 0.50 Al and 0,00 Al; the observed values for sanidine are 0.25 Al, 0.25 Al, and for microcline 0.25, 0.56 Al in 'Si₁' (0) and 'Si₁' (m), 0.07 and 0.08 Al in 'Si₂' (0) and 'Si₂' (m) respectively.

The deviations from charge balance are as follows:

Microcline 0.32
Sanidine 0.22
Orthoclase studied here 0.10
Optimum orthoclase
     (F. T. T's 'ideal orthoclase') ...   0

An interesting point arises if we consider the length of the K-O bonds. If we average the (0) and (m) atoms of microcline, to make the structures comparable, we find that from sanidine to microcline the increase in the Al content of the 'Si$_1$' site is accompanied by a decrease in the length of K-OA$_1$ (OA being linked to 'Si$_1$') and an increase in the length of K-OA$_2$ (OA$_2$ being linked to the Si-rich 'Si$_2$'). This implies an increasing strength of K-OA$_1$ as 'Si$_1$'-OA$_1$, weakens, with the converse effect for K-OA$_2$. The change in K-OA$_2$ is the greater of the two, which may perhaps be attributed to the fact that OA$_2$ has only one K neighbour and so the whole difference has to be borne by one bond, while for OA$_1$ it is shared between two.

One final very interesting point may be mentioned. On the final difference maps, near many of the atoms, there were regions with crosses or quatrefoils of positive and negative regions, corresponding to *small* elongations of Fourier peaks, probably too small to be noticed on the F map.

These did not seem to be due to absorption errors, and they could not be cured by assigning anisotropic temperature factors. On the other hand they were wiped out in the [010] projection by abolishing the plane of symmetry and allowing the two superposed atoms to move separately, and in the other two projections by abolishing the diad axis. But it did not seem reasonable to have atoms with triclinic symmetry in a monoclinic cell. In any case, the removal of the symmetry was not the *only* way to effect this cure; any model which gave two half atoms for every previously single atom would do it. It seems more reasonable to assume that what we see is an average structure. What is the ordered structure from which it is derived by the averaging process is an interesting question which cannot yet be answered.

One obvious thing to try was to take an average of two microcline unit cells in twin orientation; but no way could be found of getting the atomic positions to fit the crosses. Another is to suppose that the true cell is doubled, and there are antiphase domains small enough to wipe out the extra reflections by the effect of diffraction broadening; this could well happen if the true ordered structure were like that of celsian, where the difference reflections are extremely weak to start with. This remains a possibility, but there is no definite evidence for it.

I will quote Dr. TAYLOR's concluding paragraph:

"We finally conclude that our analysis falls short of the accuracy and resolution which migh permit a definite decision on the nature of the presumed 'average' or disordered structure represented by the orthoclase parameters [found in this work]. Such evidence as we have inclines us to the view that an attempt to discuss our orthoclase structure as though it were made up from multiply-twinned units with a well-defined microcline structure is unlikely to be physically realistic, but it leaves unsettled the possibility that orthoclase represents a faulted 14 Å structure".

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DISCUSSION

LAVES (Zurich):

The point should be stressed that the data given for «microcline» are those of *one* intermediate specimen of the continuous sanidine-microcline series.

MEGAW (Cambridge), answer:

The microcline mentioned here is that studied by Bailey and Taylor, which is now known not to be a maximum microcline. I believe that there is work in progress on a maximun microcline by Prof. Bailey at Wisconsin University. Dr. Taylor would also wish me to stress that the structural work on orthoclase reported here is on one particular material, Spencer's C, and that it cannot be assumed automatically that the results apply also to other orthoclases.

LAVES (Zurich) and GOLDSMITH (Chicago), written comment:

As it was shown by us (see our paper on «Polymorphism, order, disorder, diffusion and confusion in the feldspar», this volume), all evidence points to the fact that the sanidine-microcline transformation passes through states which are composed of submicroscopically twinned domains which are triclinic due to an Al/Si-order incompatible with monoclinic symmetry. On the other hand, it is known that the lattice geometry of small feldspar domains can be strongly modified by their environment. Thus, an average monoclinic symmetry produced by fine scale twinning of the microcline cross-hatched type may well conceal the triclinic lattice geometry, which the small twinned domains would have if they could be investigated as separate units. Thus Dr. TAYLOR's final conclusion, that such a model «is unlikely to be physically realistic» appears rather questionable. It may be pointed out that a conventional structure determination cannot give an unequivocal answer to the problem for the following reason: All the hkl (k $\neq$ 0) intensities measured and treated as monoclinic ones may actually be the sum of hkl and h$\bar{k}$l intensities of finely twinned triclinic material, which coincide on the film. To use the average of two different intensities for a structure determination as if it were representative of one intensity, must lead to wrong results as a matter of principle. A similar mistake would be made if one would try to determine the structure of low-quartz using the intensities of a sample finely twinned after the Dauphiné-law.

In the paper by JONES and TAYLOR it is stated that the material used showed weak streaks. Thus it seems probable that these streaks are of the kind which LAVES (J. Geology *58* [1950] 567) showed to be indicative of the existence of finely twinned domains of microcline character. As a matter of principle, any structure determination using such twinned

material without discussing the hkl/hk̄l-intensity ratio of the measured hkl intensities cannot represent the true atomic structure, but only an «average» structure. How nearly the true structure can be approached by such a procedure depends on the size of the domains and on their deviation from monoclinic symmetry as far as the Al/Si distribution is concerned.

In her remarks to our paper (this volume, p. 79) Dr. MEGAW states that her experiences with celsian appear to make it justifiable to ignore the «weak» streaks, as their inclusion in constructing the electron density maps would not bring about any modification of the results. We agree with Dr. Megaw that the *intensity* of the weak streaks may be ignored but not their *existence*, i.e. it is not a question of ignoring some few weak intensities, but of misusing *all* the intensities hkl with $k \neq 0$. For further discussion of the problems here involved, see the paper by LAVES and GOLDSMITH (Polymorphism, order, disorder, diffusion and confusion in the feldspars, this volume p. 71).

MEGAW (Cambridge), reply:

Refinement of a structure by successive approximations, in which average intensities or average coordinates are used in the early stages, is not «wrong… as a matter of principle» but a recognized, tried, and useful method, if used properly. It is not the method, but the experimental accuracy of the measured intensities, which sets limits to the accuracy of the final structure. Neither does the final accuracy depend on the domain size or the Al/Si distribution. I think it might be possible, with proper care, to determine the structure of low-quartz from a twinned specimen.

If, for SPENCER C orthoclase, the best available approximation to the structure does not show any experimental evidence of difference from a monoclinic structure but does show differences from any combination hitherto tried of superpositions of known microcline twins, how can it legitimately be said that *this* «evidence points to the fact that» SPENCER C orthoclase is «composed of submicroscopically twinned domains which are triclinic»?

The alkali feldspars as ionic structures

by R. B. FERGUSON (*).

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ABSTRAT (**)

New relationships among the alkali feldspars have been proposed by FERGUSON. TRAILL and TAYLOR (Acta Crystallographica, 1958, **11**, 331) to account for the observed Al-Si distributions in the two low-temperature feldspars whose structures have been refined, low albite and intermediate microcline. Consideration of these structures and those of the two high-temperature forms which have also been refined, high albite and sanidine, leads to the conclusion that the atoms in these minerals behave as ions, and that the most stable low-temperature alkali feldspars are in general, those that have the most satisfactory electrostatic charge balances. For slowly cooled pure Na and pure K feldspars respectively, these prove to be largely (but not fully) ordered low albite (triclinic) and slightly ordered orthoclase (monoclinic). On this view, the Al-Si ions which are disordered in the high-temperature forms presumably because of thermal motion, migrate in such a way as to offset the charges given to certain oxygen ions by the Na^+ or K^+ ions.

When appreciable amounts of both Na and K are present in a slowly cooling alkali feldspar, microcline is thought, from the following considerations, to result. Crystal-chemical considerations, heating experiments by E. SPENCER on microperthites, and recent alkali-ion exchange experiments on alkali feldspars all suggest that, in a cooling alkali feldspar, Al-Si migration (ordering) will take place at a much higher temperature than K-Na segregation (perthitization). Since the Al-Si ions migrate in a manner that is determined by the type of alkali ion present and since the alkali ions will likely be disordered at the high temperatures at which the Al-Si ions migrate, the resultant Al-Si framework will reflect the K:Na ratio at the high temperatures: for predominant K it will be similar to slightly ordered monoclinic orthoclase, and for predominant Na it will be similar to largely ordered triclinic low albite. If sufficient Na is present, the framework will have a triclinic Al-Si distribution, and when K-Na segregation takes place at some lower temperature, triclinic microcline with an appreciable charge unbalance will result. Thus this theory indicates that there is a series of low-temperature K feldspars, varying from slightly ordered orthoclase formed in the presence of little or no Na, through intermediate microcline, to largely ordered maximum microcline formed in the presence of considerable excess of Na over K. This origin for microcline accounts in a quantitative way for the Al-Si distribution found by BAILEY and TAYLOR (Acta Crystallographica, 1955, **8**, 621) for an intermediate microcline, and it suggests that the monoclinic-to-triclinic change in low-temperature K feldspars occurs at an original alkali feldspar composition of about 20 % $NaAlSi_3O_8$. Since some petrologists have concluded that the process of K-Na segregation may extend beyond the perthite stage to give a fairly pure K feldspar and a high Na plagioclase exinting side-by-side in the rock, no correlation is to be expected for at least some orthoclases and microclines between their monoclinic or triclinic character and the Na-content of the actual specimen. These relationships are much different from those proposed by GOLDSMITH and LAVES who assume that the most stable low-temperature alkali feldspars are those most fully ordered with respect to Al-Si. Some of the many implications of the present theory will be discussed. (Appears as «The low temperature phases of the alkali feldspars and their origin» in Canadian Mineralogist, 1960.)

(*) As the speaker was not able to attend the meeting the paper was read by tittle only.
(**) Reprinted from the program, distributed in Copenhagen, August 1960, as no manuscript was received.

Atomic, chemical and physical factors that control the stability of alkali feldspars [1]

by J. V. Smith [2].

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ABSTRACT

At constant temperature, pressure and composition the most stable form will be that in which the Gibbs free energy (G) is a minimum. In the expression $G = U + PV — TS$, U will predominate at low temperatures and TS at high temperature. The internal energy (U) of the ordered phase can be expected to be lowest because the disordered arrangement will lead to juxtapositions of Al atoms that unbalance the ionic forces (Pauling's second rule). The disordered form will have the highest entropy because of the contribution from the permutations of the different possible Si, Al arrangements and the extra vibrational modes of the lattices. At low temperatures the most stable state will be the ordered one, while at high temperatures the stable state *may or may not* be the disordered state depending on whether the difference between the internal energies is less than the entropy term. In alkali feldspar with a 1:3 ratio of Al:Si the internal energies of the extreme states should be fairly similar because there will be few juxtapositions of Al atoms in the disordered state. In celsian and anorthite the internal energies should differ considerably because of the many oxygen atoms shared by two Al atoms in the disordered state. This qualitative argument agrees with the observation that, while disordered high-sanidine is the stable form of alkali feldspar at high temperature, anorthite is probably ordered at all temperatures.

The relative importance of local order [3], distant order and twin boundaries in governing the nature of microcline is discussed. Twinning is an ordering mistake repeated consistently along the twin boundary in contrast to disorder which occurs randomly. In maximum microcline there probably is complete distant order with ordering mistakes only at albite and pericline twin boundaries. Intermediate microclines occur either with diffuse or fairly sharp X-ray reflections. For the latter there is probably partial distant order over large domains that are separated by twin boundaries. For the former, two extremes are possible: close twin boundaries with complete order in each domain; and remote twin boundaries with variable order in each domain.

Solid solution between Na and K ions will probably lead to an extra difference in the free energy of the ordered and disordered phases, resulting in disorder occurring at lower temperatures for intermediate compositions. Small amounts of divalent ions should play important roles in ordering of alkali feldspars, because the consequent change of Si:Al ratio will disturb the ordering sequence. Consequently authigenic microcline should be able to form at a higher temperature than its igneous equivalent which will contain An and Ab in solid solution.

INTRODUCTION

In this paper, and the following one "Structural variations in alkali feldspars" by MacKenzie and Smith, thermodynamic, crystal-structural, controlled-synthesis and petrologic considerations are reviewed and integrated with the aim of producing a phase diagram for the alkali feldspars. In addition, kinetic factors are evaluated so that an interpretation can be given of the common growth and persistence of metastable varieties. The thermodynamic and crystal-structural approaches will be adopted in this paper, with particular emphasis on the details of Al-Si disor-

der and the consequent effects on the thermodynamic funtions. In the second paper, which should be read in sequence, data obtained from controlled-synthesis experiments and from petrologic investigations are considered, and a final conclusion reached on the basis of all four types of evidence.

Primarily these two papers are review articles based on the cumulated publications of many workers, but for brevity, no attempt has been made to trace in detail the development of ideas from the simple beginnings to the present, more sophisticated states. Some further extensions, not hitherto published, are given: the more important of these involve the possible effects of local order, and the nature of the truly stable phase diagram. In writing these articles, considerable help has been gained from informal discussions with workers at Cambridge, Zürich and Chicago, to whom we wish to acknowledge our thanks.

GENERAL THERMODYNAMIC CONSIDERATIONS

At constant temperature, pressure and composition, the truly stable form will have the minimum Gibbs free energy (G). The presence of the PV term in the expression $G = U + PV - TS$ will favour the stability of the denser, ordered form with respect to the disordered forms when the pressure is increased: this effect will be small because of the close similarity of the volumes. The internal energy (U) of the ordered form of feldspar can be expected to be lower than that for the Si-Al disordered equivalents, because only one arrangement can have the lowest internal energy, and this arrangement will be repeated to give the ordered structure. Consequently at absolute zero, where the entropy term, TS, disappears, the most stable form will be ordered. Disordered forms will have higher entropies than the ordered form because of the contributions from the permutations of the different possible Si-Al arrangements and from the extra vibrational modes of the lattice. Consequently the TS term in the above equation will increasingly favour the stability of the disordered form as the temperature is raised. Working in the opposite direction will be the U term, because the disordered form can be expected to have a higher internal energy than the ordered form, as a result of the disturbance of the chemical forces produced by disorder. Consequently, the high-temperature form may or may not be disordered depending on whether ΔU is greater or less than $T \Delta S$. Unfortunately in the present rudimentary state of knowledge of chemical forces in crystals, it is not possible to make quantitative calculations of either U or S, and qualitative arguments must be used.

Substitutional disorder of K and Na should lead to relatively small changes of U between the ordered and disordered forms because the Na-O and K-O polyhedra are large and often irregular. Thus disorder should be attained at relatively low temperatures. Positional disorder of Si and Al should have much larger effects on U because of the high strength of the bonds and the large percentage change of bond length and ionic charge. This difference in U should grow rapidly as the Al/Si ratio increases up to unity because of the larger number of oxygen atoms joined to two aluminiums. The experimental observations that Al-Si disordered forms of $KAlSi_3O_8$ and $NaAlSi_3O_8$ exist in the solid state while anorthite, $CaAl_2Si_2O_8$, is certainly ordered up to 1400°C., and possibly up to the melting point, are consistent with this idea.

So far substitutional disorder of Na-K and positional disorder of Si-Al have been treated as separate phenomena, but in all alkali feldspars except the very pure, authigenic specimens they will occur together. It is expected that the two types of disorder will

cooperate so that at any particular temperature Al-Si disorder will be achieved more easily in mixed Na-K specimens than in the pure end menbers. Two factors should bring about this result: first there will be contributions to the entropy term from both the Na-K and Si-Al disorders, and secondly the difference in the U terms of the Si-Al ordered and disordered forms of a particular Na-K mixed feldspar should be less than for the equivalent endmembers because irregularities in the chemical forces caused by one form of disorder should promote irregularities in the pattern of the other atoms. This argument is consistent with the observation that microcline-low albite perthites are harder to homogenize than sanidine-anorthoclase perthites (TUTTLE and BOWEN, 1958) (4), and with the evidence that the two phases of the natural sanidine, orthoclase and microcline series of perthites approach progressively, on the average, the compositions of the pure end-members.

CRYSTAL-STRUCTURE DATA AND RELATED OBSERVATIONS

At the time of writing, the following structural determinations have been completed: high-sanidine by COLE, SÖRUM and KENNARD (1949), an intermediate microcline by BAILEY and TAYLOR (1955), high albite and low albite by FERGUSON, TRAILL and TAYLOR (1958). Data for orthoclase will be presented at this symposium by JONES and TAYLOR. All these structures have been determined at room temperature and atmospheric pressure and it should be borne in mind that, while the Al-Si distribution will be unaffected by quenching, the details of the atomic positions and vibrations, especially for Na and K. atoms, will vary considerably with temperature: for example, the cell angles of high albite change by several degrees when heated up to its melting point. Probably the major change will be increased vibration of the Na and K atoms, especially for the former, with vibration becoming more isotropic than that found by FERGUSON et al. in the room-temperature determinations.

The diffraction studies give evidence on the distant order of Si-Al (but not on the local order), and the

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(4) Since this was written, Prof. F. LAVES has described to the writers, experiments in which he and Prof. J. R. GOLDSMITH found easy homogenization of microcline-low albite perthites. If a single crystal of microcline with a band of perthitic vein albite which originally shows clear domains of albite twin relations is heated, the following can be observed: those albite domains of which the Al/Si-distribution is in phase with one of the microcline single crystal orientation vanish. The other set homogenizes too but stays visible as a row of separate microcline domains with extinction angles symmetrical to the other set which became indistinguishable from the remaining microcline single crystal due to the homogenization process. Consequently there is some doubt as to the significance of the interpretation here proposed by the writers.

relative occupancy of any site is based on the measured Si, Al-O distances and their interpretation in terms of a linear relation between standard values for Si-O and Al-O. Recently SMITH (to be published) on the basis of much better data has revised standard values from Si-O 1.60 ± 0.01 and Al-O 1.78 ± 0.02 (SMITH, 1954) to 1.603 ± 0.003 and 1.77 ± 0.01. Measurements on high sanidine and intermediate microcline were made by very accurate three-dimensional syntheses with σ (Si-O) = 0.008 Å while the others were made by less accurate two-dimensional syntheses with σ (Si-O) = 0.02 Å. Averaging of the four Si-O values for each tetrahedron reduces the error of the mean by about one-half. Because of the possibility that mean Si, Al-O values do not depend solely on the Si, Al ratio, it is not possible to calculate the precision of an estimate of Si, Al content from the observed Si, Al-O distances. However, the consistency of the values of Si, Al-O for the different tetrahedra in the disordered structures suggests that this uncertainty is not more than the equivalent of 0.005 Å. Consequently it is suggested that estimates of Si, Al content for the 3 D determinations are accurate to 0.05 and for the 2 D determinations to 0.09. The former one will be too pessimistic if Si, Al-O values depend only on Si, Al ratio, while the latter will be too optimistic if overlapping of peaks in projections causes systematic errors.

High sanidine and high albite gave distances consistent with complete distant disorder. The intermediate microcline gave values indicating Al contents of 0.25, 0.58, 0.05 and 0.07 (total 0.95) in the four independent tetrahedra, whereas low albite gave — 0.08, 0.83, 0.08 and 0.20 (total 1.03). Eagerly awaited are determinations of maximum microcline by BAILEY and a more accurate three-dimensional refinement of low-albite by FERGUSON.

Additional evidence on Si, Al ordering has been obtained from infra-red absorption patterns (LAVES and HAFNER, 1956: HAFNER and LAVES, 1957), nuclear magnetic resonance (BRUN, HAFNER, HARTMANN, LAVES and STAUB, 1960) and in a rather less direct manner from optic axial angle measurements (SPENCER, 1937; TUTTLE, 1952 a, etc.), and studies of cell dimensions and powder patterns (MACKENZIE, 1952: etc.).

Si-Al ORDER IN K-FELDSPAR.

From these measurements it seems reasonable to deduce that maximum microcline, as defined by MACKENZIE (1954), is more ordered than BAILEY's intermediate microcline, and indeed may be completely ordered. Scattered reports of isomicrocline and isoorthoclase (BARTH, 1933; TSUBOI, 1936; KAZAKOV, 1956) with optic axial angles even more extreme than maximum microcline require confirmation by other techniques before they can be accepted. Such a confirmation would probably require a redefinition of maximum microcline, but because of the difficulty of measuring optic axial angles of microcline, and the possibility of unusual chemical compositions, there is no need at the present time to believe that the present maximum microcline is not the most ordered form of K-feldspar.

HAFNER and LAVES (1957), followed by BARTH (1959), have suggested that there are different ways of passing from high sanidine to maximum microcline, ranging between the extremes of (a) a one-step process in which three of the tetrahedra lose their Al atoms at an equal rate to the other tetrahedron, and (b) a two-stage process in which two of the tetrahedra lose their Al equally to the other two which gain equally, followed by loss of all the Al from one of the latter two tetrahedra to the other one. LAVES (1960) has amplified these views and extended them to albite (5). The present authors agree with this theory of multiple paths, and indeed had a paper on this subject in preparation at the time of publication of the HAFNER and LAVES paper. From this unpublished paper, some optical evidence that supports the theory will be quoted.

In the one-step process, the feldspar becomes triclinic as soon as any ordering occurs, whereas in the second one, the feldspar remains monoclinic throughout the first stage and only goes triclinic during the second step. There is good reason to believe that the optic axial angle (2 V) is a function, not necessarily linear, of the development of order, while the rotation of the optic axial plane from the positions with monoclinic symmetry is a measure of the unbalance of order between the pairs of tetrahedra related by symmetry in the monoclinic feldspars. If this is correct, all specimens should give optic properties lying between the "triangle" formed by the extreme values for high-sanidine, maximum microcline and the intermediate product of the two-step trend. This is shown schematically in Fig. 1.

Igneous specimens give optic properties that lie on a two-stage trend (SPENCER, 1937: TUTTLE, 1952 a, etc.) with those lying between high sanidine and orthoclase having monoclinic symmetry and those from orthoclase to maximum microcline triclinic geometry. From this, orthoclase is deduced to be the intermediate product of the two-stage process. (Most of these feldspars contain considerable sodium in substitutional disorder but this does not invalidate the deduction).

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(5) McCONNELL and McKIE (1960) have shown from an analysis of the synthesis data on albite obtained by MacKENZIE (1957) that the activation energy of the formation of intermediate albites from high albite depends on temperature. McKIE (personal comunication) pointed out to us that he and McCONNELL though that this could be explained by a change in the coordination of the sodium atom. He agreed with us that it could also be explained by a two-stage Al-Si ordering process and that it was possible that both processes might occur together.

K-feldspars with the adularia habit, obtained characteristically from low-temperature environments, give
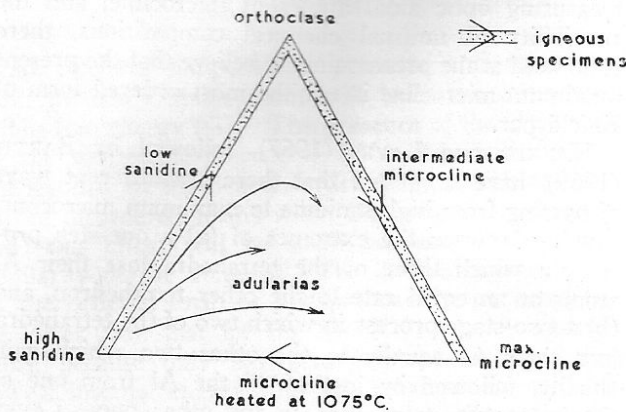
Fig. 1.—Schematic diagram showing different paths between the three extreme varieties of K-feldspar; high sanidine, orthoclase and maximum microcline. See text for detailed explanation. This diagram is similar to Fig. 2 of BARTH (1959), but the present authors, in agreement with HAFNER and LAVES (1957), believe that orthoclase does not have the extreme values of Al/Al + Si for the four tetrahedra, 0.5, 0.5, 0.0 and 0.0, listed in BARTH's Fig. 2.

optic properties lying in-between the three end-members (CHAISSON, 1950) and it is reasonable to suppose

that they crystallized as sanidine and took a variety of paths to maximum microcline, with the majority left in intermediate states (Fig. 1). Upon heating at 1075°C, microcline transforms directly to high sanidine, giving optical properties consistent with the one-step trend (MACKENZIE, 1953, und unpublished).

In Fig. 2 are shown possible variations of the Al-content in the four tetrahedra that are consistent with these optical observations. Tetrahedra a_1 and a_2, b_1 and b_2 are respectively related by monoclinic or pseudomonoclinic symmetry. In the two-stage trend Fig. 2 a), a_1 and a_2 lose Al to b_1 and b_2 as the feldspar changes from high sanidine through low sanidine to orthoclase. After this b_1 begins to lose Al as the feldspar passes through intermediate microcline to maximum microcline. The curves are adjusted to pass through the values given by BAILEY and TAYLOR for their particular intermediate microcline. Orthoclase has been assumed to have about 0.15 Al and 0.35 Al in the two independent types of tetrahedra, but somewhat different values would be possible (6). In Fig. 2 b, the variation of order for maximum microcline heated at 1075°C. is shown, and in the absence

(6) JONES and TAYLOR found values of Si, Al-O 1.652 and 1.633 Å for the two independent tetrahedra which correspond to Al values of 0.29 and 0.18.
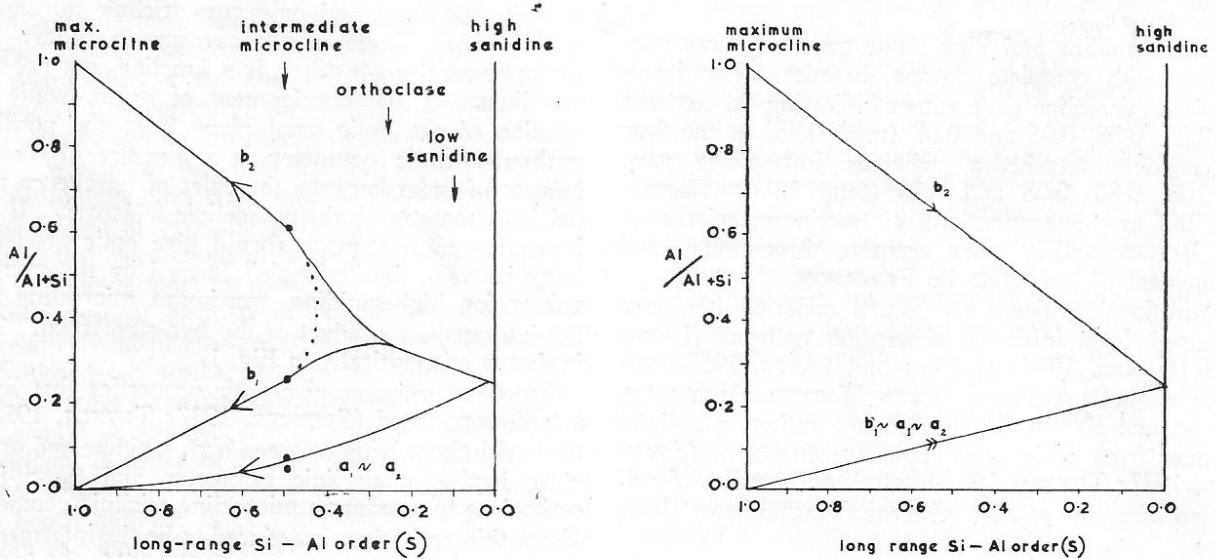
Fig. 2.—Suggested variations of Al-Si order in K-feldspars. Diagram (a) shows the possible variation in the two-stage trend for specimens cooled down in igneous rocks, while (b) is for the non-equilibrium conversion of maximum microcline to high sanidine at 1075°C. The distant order function (S) is defined as $\sum_{i=1}^{i=4} \frac{|0.25 - S_i|}{1.50}$ where S_i is the distant order, Al/Al + Si, in the four different types of tetrahedra. The value of 1.50 corresponds to perfect order in maximum microcline. The four curves labelled a_1, a_2, b_1, and b_2 show the amounts of Al in the four tetrahedra labelled Si_2 (001), Si_2 (mOi), Si_1 (mOi) and Si_1 (001) by MEGAW (1956). These diagrams are similar to Figs. 15 and 16 in the paper by HAFNER and LAVES (1957). The positions of the curves in (a) are arbitrary and based on the values obtained by BAILEY and TAYLOR for an intermediate microcline. Theoretically, it is possible to have ordering in orthoclase of 0.0, 0.0, 0.5 and 0.5 for a_1, a_2, b_1 and b_2, respectively, but this would mean that in going from orthoclase to intermediate microcline tetrahedra a_1 and a_2 would have to gain Al again. The particular curves assumed here assume that orthoclase has an Al-distribution of 0.15, 0.15, 0.35 and 0.35, but considerable deviation from these values could occur, as given for example by the dotted curves.

of any direct measurements of the Si-Al order, the ideal one-stage trend is shown. Adularias would be expected to follow paths intermediate between the two-stage and the one-stage (reversed) trends shown in Fig. 2.

Most X-ray photographs of K-feldspar show one or two types of diffuse reflections. As the observations have been summarized by SMITH and MACKENZIE (1959, p. 1180-1185), only the more important of the results will be given here. Some specimens of K-feldspar, especially of the adularia type, show diffuse X-ray reflections centered on positions with (h + k) odd. These reflections have been independently interpreted by LAVES and SMITH (to be published in a joint paper) as the result of movement of Si and Al atoms occurring without the coherence required to maintain the C face-centering. No igneous specimens examined by SMITH and MACKENZIE, except for some pegmatitic specimens from the SPENCER series, show these primitive reflections and from this it may be deduced that there is correlation between movement of atoms related by the C fase-centering. Adularia specimens characteristically show this type of reflection, but whether all adularias give them is not known. It is reasonable to suppose that the presence of these reflections is an indication of non-equilibrium movement of Si-Al atoms, which confirms the belief that adularia, because of its low temperature of formation, undergoes non-equilibrium movements of Si and Al atoms, whereas the igneous specimens follow an equilibrium or near-equilibrium path. The variation of Si, Al pattern in adularia must, of course, be more complicated than that given earlier: actually eight, not four, independent tetrahedra need to be considered.

All K-feldspars except maximum microcline and high sanidine show very weak diffuse reflections, elongated along b*, and centered on the main reflections with C face-centered symmetry. These reflections are probably stronger in orthoclase than in low sanidine, but accurate intensity measurements are needed before this statement is proved. The cause of these reflections will be discussed later in the section dealing with the variation of order with distance.

Si-Al ORDER IN Na-FELDSPAR

As most the evidence concerning the transitions between the different forms of albite comes from studies of naturally-occurring feldspars, and particularly from heating and synthesis studies, it is appropriate to discuss most of the aspects of the polymorphism of $NaAlSi_3O_8$ in the next paper. However, it is convenient to make here a few suggestions concerning the Al-Si order.

The details of the Al-Si order in Na-feldspar are more uncertain than those for K-feldspar. The measurements of FERGUSON, TRAILL and TAILOR on low-albite are tantalizing in that they are consistent with incomplete order, but have a random error so large that the deviation from complete order is only on the verge of significance. On the basis of these observations, FERGUSON et al. have proposed that electrostatic charge balance controls the Si-Al ordering of feldspars, and have proposed that orthoclase, and not microcline, is the stable form of K-feldspar at low temperature. MACKENZIE and SMITH (1959) have criticized both the theoretical basis and the practical conclusions of theory, to which FERGUSON, TRAILL, and TAYLOR (1959) made a reply. A further paper on this theory of charge balance has been submitted by FERGUSON to this symposium, and due to his kindness in submitting and advance copy to us, we will be able to comment later in these two papers on this hypothesis.

Although there is no conclusive evidence concerning the possibility of different ordering paths from high albite to low albite, it seems reasonable to suppose that these will occur. The majority of high-temperature sodium-rich feldspars contain so much calcium that considerable variation of Al/Si ratio occurs during inversion. Consequently it is not possible to use these natural specimens to give information on the ordering of pure $NaAlSi_3O_8$. Indeed the available evidence of natural feldspars suggests that some, and perhaps most, of the igneous specimens change discontinuously from a disordered anorthoclase or sodium-rich sanidine perthite to an ordered albite (or oligoclase) perthite, whereas synthetic albites, when equilibrium is established, show a continuous transition from high albite near 1000°C. to low albite near 450°C. (MACKENZIE, 1957). Analogous to adularia is pericline, the variety of albite found in low-temperature environments. Pericline specimens are extremely pure and show variable optics that might well result from intermediate states and paths of order analogous to those previously described for adularia. Further investigations of these specimens is desirable.

The role of monalbite is rather uncertain. In the next paper reasons are given for doubting whether the type of monalbite that is monoclinic at room temperature after quenching has a temperature range of stability. Whether or not this is so, it appears that monalbite is formed at higher temperatures than the high albite formed at 900-1000°C. by MACKENZIE, and the high albite whose crystal structure was accurately measured by FERGUSON, TRAILL and TAYLOR. The higher temperature for formation of monalbite would suggest a structure more disordered than that of high albite, and if high albite has complete distant order, as suggested by FERGUSON et al. it is hard to suggest an ordering scheme for monalbite. LAVES (1960, Fig. 7) however, has suggested that high albite is not fully disordered and that conversion to

monalbite involves further disordering, a possibility that is within the range of experimental error of FERGUSON et al. 's data. A more accurate three-dimensional synthesis of high albite and a structural analysis of monalbite would permit a test of this idea. A new alternative hypothesis is that while both high albite and monalbite have complete distant disorder, high albite has local order in contrast to the local disorder in monalbite. This suggestion could be tested by three-dimensional syntheses of high albite and monalbite, followed by an analysis of the regions between the sharp X-ray reflections to give information on the local order.

Until the status of monalbite is established by further experiments the authors prefer not to use the complex nomenclature for albite proposed by LAVES, and interested readers are referred to his 1960 paper for full details.

VARIATIONS WITH DISTANCE OF Al-Si ORDER. KINETICS OF ORDERING

1. *General considerations.*

Much attention has been paid by metallurgists to order-disorder phenomena in alloys, and considerable observational and theoretical progress has been made (see, for example, the review by GUTTMAN (1957)). Similar studies of feldspars are in a much more rudimentary state, partly because of the greater complexity of the feldspar structure, and partly because it has been necessary to establish the broader pattern of the phenomena before going into fine details. Consequently it is necessary to treat the details of order mainly in a theoretical manner using the ideas developed for the alloy systems as a guide. Such use of analogy must be treated with circumspection because of the major difference in the chemical forces, and only after a long series of detailed experimental studies, which, it is hoped, will appear during the next decade, will it be possible to give a definitive analysis of order in feldspar. The following treatment owes much to the papers of GOLDSMITH and LAVES (1954 a, b) and MEGAW (1959) among many others, but because of some differences of outlook, it is recommended that these papers be read if it is wished to ascertain the detailed views of these authors.

Ordering of Si and Al atoms in feldspars is not merely a matter of arranging different atoms on a fixed set of lattice positions. Each movement of Si and Al atoms involves distortion of the framework and movements of the Na and K atoms. Such displacements affect neighbouring parts of the structure with an amplitude that decreases with distance. In an ordered structure the displacements will cooperate so that a structure with maximum geometrical distortion from that for the disordered forms will be produced. In disordered structures the pattern of Si-Al atoms will vary and the potential distortions will act in different directions and not cooperate to give maximum distortions. Furthermore the atomic coordinates, chemical forces and thermodynamic functions of a disordered structure will not be the average of those for the different possible ordered structures into which the ordered structure could be broken. It is for this reason that it is important to consider the variation of order with distance, for only when ordering is maintained over fairly large volumes will the forces in these volumes be able to cooperate to give large geometrical distortions. The following detailed suggestions concerning the order in alkali feldspars are almost completely speculative and designed more to
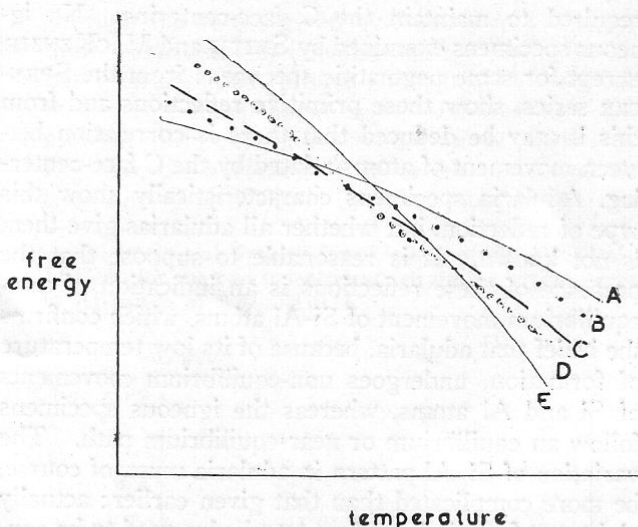
Fig. 3.—Suggested relation between the free-energy curves for the different states of Si-Al order: A complete order, B about three-quarters ordered, C about half ordered, D about one-quarter ordered and E completely disordered. These five curves are just a few out of the infinite number possible between the two extreme curves for complete order and complete disorder. Each curve will have a free energy less than all the other curves at one particular temperature resulting in a continuous transition from the ordered state at low temperatures to the disordered one at high temperatures. In this diagram, strain energy from anti-phase domain boundaries is ignored: if the strain energy becomes significant some modification is required along the lines suggested by UBBELOHDE (1957).

stimulate further research than to give answers to certain important problems. Nevertheless it is hoped that the plausibility of the ideas will give a reasonable chance that they are, in fact, not too far from the truth.

It will be assumed here that the ordering process is not of the first-order and that the free energy curves have the form shown in Fig. 3 giving a continuous transformation. (This type is thought to be more plausible than those given by EHRENFEST (1933) and UBBELOHDE (1957) and will be discussed by SMITH

in another publication). There are both theoretical and experimental reasons for this: first, the experiments of MacKenzie (1957) suggest that the equilibrium form of albite varies continuously with tempe-

consequently a transition will propagate more easily. In feldspars the Si and Al atoms are linked through oxygen atoms and therefore a continuous transition can be expected.
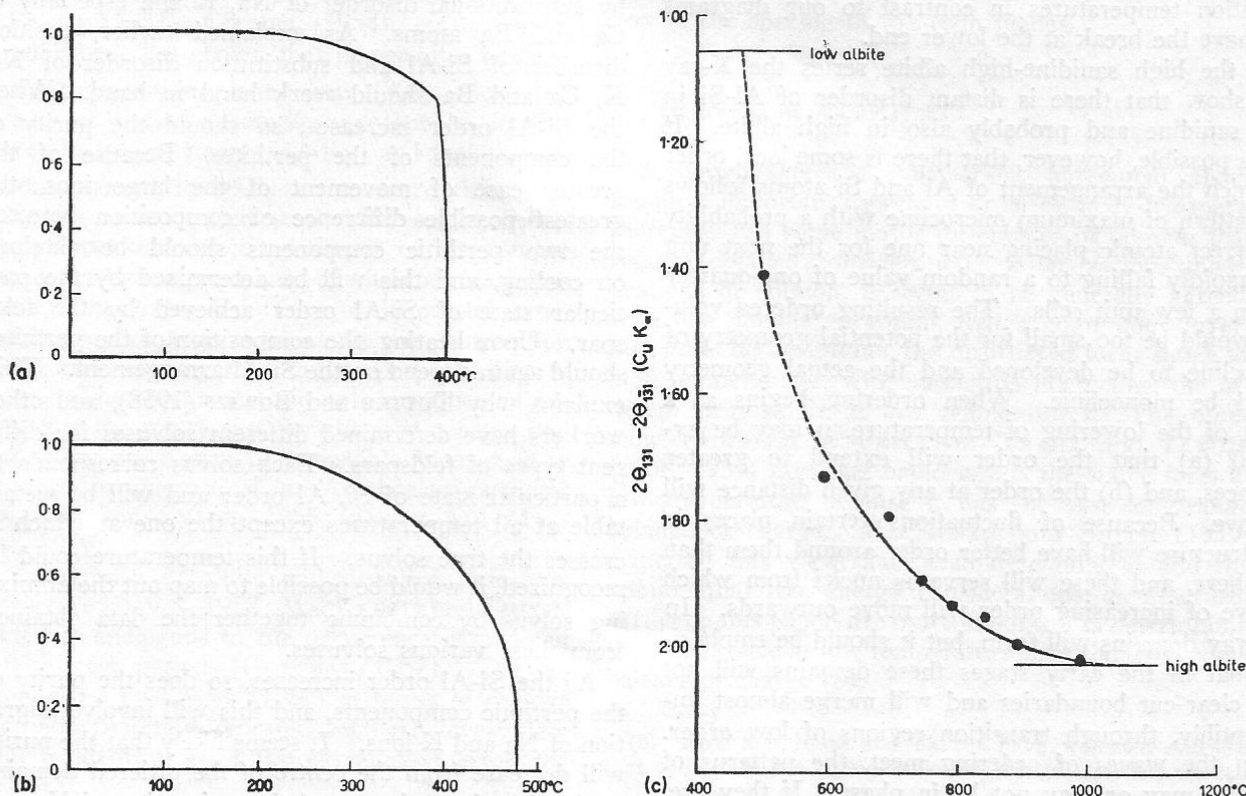
Fig. 4 (a).—Long-range order coefficient (S) versus temperature for Cu₃Au after Keating and Warren (1951), an example of a first-order transition. Note the continuous forewarning before the discontinuity.

(b) Long-range order coefficient (S) versus temperature for CuZn (β-brass) after Chipman and Warren (1950), an example of the continuous transition.

(c) Variation of order with temperature for synthetic NaAlSi₃O₈ (MacKenzie, 1957). The function 2θ (131) -2θ $(1\bar{3}1)$ is taken to be a measure of the Si-Al order with a value of 1.07 for low albite and 2.03 for high albite. The values for 2θ (131)-2θ $(1\bar{3}1)$ are extrapolated to infinite time from the values obtained for synthesis over various periods.

rature (7) and secondly, study of alloys suggests that when the order-related atoms share first neighbours a first-order transition occurs while those that do not share first neighbours are related by a continuous transition (Fig. 4). (Many first-order transitions appear to begin with a continuous change (a "forewarning") and then become discontinuous). The fundamental reason for the effect of coordination would seem to be that in the first-coordination type, exchange of atoms will affect neighbours to a greater degree than in the second-coordination type and

Unlike alloys where the order tends asymptotically to perfect order with a critical temperature for complete disorder, MacKenzie's work on high albite suggests that the opposite occurs with an asymptotic approach to the completely disordered state (Fig. 4). However it is possible that there is neither a sharp beginning nor a sharp ending of order and that the plot of distant order versus temperature has a sigmoid shape. As there is no experimental data on the low-temperature side of the Al-Si transitions in feldspars it is not possible to decide wich alternative is correct, and in the absence of such data a sharp beginning of disorder will be assumed, as shown by the extrapolation in Fig. 4. Another possibility is that there is considerable hysteresis in the transition, as a result of the surface energy between domains, and that this

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(7) McConnell and McKie (1960) have shown from an interesting kinetic analysis of MacKenzie's data that there is a break in the plot of the rate constant against temperature. However the equilibrium product has cell dimensions that appear to vary continuously with temperature.

leads to a reversed sigmoid transition for the upward transition. LAVES (1960, Figs. 5 and 7) has assumed the alloy type of variation for both K-feldspar and Na-feldspar, so that his diagrams have discontinuities in the order at the upper end of the range of transition temperatures in contrast to our diagrams that have the break at the lower end.

In the high sanidine-high albite series the X-ray data show that there is distant disorder of Al-Si in high sanidine and probably also in high albite. It seems possible, however, that there is some local order in which the arrangement of Al and Si atoms follows the pattern of maximum microcline with a probability of correct atomic placing near one for the next unit cell, rapidly falling to a random value of one-quarter within a few unit cells. The resulting ordered volumes would be too small for the potential geometry of microcline to be developed and the actual geometry would be monoclinic. When ordering begins as a result of the lowering of temperature, it may be expected (a) that the order will extend to greater distances, and (b) the order at any given distance will improve. Because of fluctuations certain places in the structure will have better order around them than elsewhere, and these will serve as nuclei from which a wave of increasing order will move outwards. In this way domains will form, but it should be emphasized that in the early stages these domains will not have clear-cut boundaries and will merge almost imperceptibly, through transition regions of low order. When the waves of ordering meet, the patterns of ordering may or may not be in phase. If they are, two domains will coalesce to form one, and if not, an "antiphase domain boundary" will be produced. Such boundaries will be very irregular at first but will gradually become more regular so as to satisfy the thermodynamic need to lessen the strain energy at the domain boundaries. When the surfaces become regular, and the domains are wider than the resolution of the microscope, they will be recognized as composition planes of albite and pericline twins. The common observation of the regularity of the twin boundaries with the two twin types adopting the (010) plane and rhombic section as composition planes shows that the need for the strain energy at the boundary to be minimized is quite important.

The minimum strain energy of a domain occurs, of course, in a single crystal, but once domain boundaries have been formed it will be hard for them to disappear because this involves reversal of ordering in all out-of-phase domains. Two factors should help to increase domain size: the first, stress (TUTTLE, 1952 b) is probably the most potent because the formation of cracks and dislocations across domain boundaries should help to provide activation energy. Evidence for the efficacy of stress is available from the petrologic studies of PHEMISTER and BUDDINGTON, quoted by TUTTLE (p. 121). The second, presence of divalent Ca and Ba ions, should have an effect because movement of these ions during the formation of perthites ought to aid corresponding exchanges of Si and Al atoms.

Development of ordering is probably complicated by substitutional disorder of Na, K and especially of Ca and Ba atoms. As explained earlier, position disorder of Si-Al and substitution disorder of Na, K, Ca and Ba should work hand in hand. When the Si-Al order increases, so should the purity of the components of the perthites. Because of the greater ease of movement of the large ions, the greatest possible difference of composition between the two perthitic components should be obtained on cooling, and this will be determined by the particular state of Si-Al order achieved by the feldspar. Upon heating, the composition of the perthites should again depend on the Si-Al arrangement. This explains why TUTTLE and BOWEN (1958), and other workers have determined different solvuses for different types of feldspars. Each solvus corresponds to a particular state of Si, Al order and will be metastable at all temperatures except the one at which it crosses the true solvus. If this temperature could be recognized, it would be possible to map out the unmixing solvus by combining together the data obtained from these various solvuses.

As the Si-Al order increases, so does the purity of the perthitic components, and this will involve migration of Na and K ions. It seems likely that the purity will decrease from the centre of the ordered domains to the domain surfaces and that migration of Na and K ions will take place predominantly along these boundaries.

Calcium atoms probably have major effects on the Si-Al ordering because of the necessary upset of the Si-Al order when extra Al atoms, charge-linked to the Ca atoms, occur in the structure. In natural albites, the ordering process is quite different from that of the pure synthetic material. MACKENZIE's syntheses of albite, though not conclusive, are consistent with a continuous inversion, whereas the natural specimens show a sharp break from anorthoclase (about Or_{20} $(Ab + An)_{80}$) to albite-oligoclase (about Or_{0-5} $(Ab + An)_{100-95}$)). Probably the large change in the Ca content encourages a more discontinuous transition in the natural specimens. In microclines there must be considerable variation in the details of the ordering for the relation between the sharpness of the reflections, which depends on the domain size, and the geometry, which depends mainly on the distant order is not single-valued (SMITH and MACKENZIE, 1959). Thus it seems clear that there is no direct relation between the domain size and the perfection of order. It is here suggested that variation in the content of Ca and Ba atoms may well be responsible for this variability. Micro-probe X-ray excitation

analysis if selected specimens, planned for the near future, should provide a crucial test of this suggestion.

The presence of strain between the components of perthites has been shown dramatically from observations that the $(\overline{2}01)$ spacings of some perthites give values outside the limits set by pure K- and Na feldspar (LAVES (1952), COOMBS (1954), etc.). SMITH (to be published) has shown that in perthites associated along composition planes near $(\overline{8}01)$, those cell dimensions of the two components that lie in this plane are identical or nearly identical and that the cell dimensions normal to $(\overline{8}01)$ differ more than they would in the unassociated state. He suggests that to a first approximation the volumes of the components of a perthite depend only on the chemical composition and that extra distortions of the crystal structure occur to give a good fit along the composition plane and an even bigger difference perpendicular to this plane. The resultant strain will introduce an extra term into the expression for the free energy, and will lead to the persistence of metastable forms such as anorthoclase in microcline- and orthoclase-perthites (MACKENZIE and SMITH, 1955; SMITH and MACKENZIE, 1959).

The occurrence of albite and pericline twin-type superstructure (LAVES, 1952; MACKENZIE and SMITH, 1955, etc.) is analogous to the occurrence of ordered alloys with large periods (GUTTMAN, 1957). The explanation given by LAVES (1952) in terms of regular polysynthetic twinning repeated regularly every few unit cell is identical with the explanation given for alloys though expressed here in different terms. In actual practice most feldspar specimens that have this superstructural are not strictly regular and many gradations between simple twinning and perfect superstructure have been observed. LAVES has explained that this structural irregularity can result from variation in the spacing of the twin planes.

2. Ordering in K-feldspars.

Although there is considerable agreement about the most important aspects of ordering in K-feldspars, there are still some major differences of opinion that require detailed consideration. After various modifications of opinion, it seems to be generally agreed, with one notable exception, that a continuous inversion links high-sanidine, the disordered form stable at high temperatures, with maximum microcline, the ordered form stable at low temperatures. The other view, expressed by FERGUSON, TRAILL and TAYLOR (1958, 1959) says that orthoclase is the stable form at low temperature because it has the best long-range balance of charge. MACKENZIE and SMITH (1959) criticized this view, and wish here only to add the opinion that free energy considerations, as described earlier in this paper, are more important in determining the form stable at low temperature than the long-range balance of charge (8).

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(8) Now that JONES and TAYLOR have presented evidence that orthoclase has considerable long-range disorder, we can
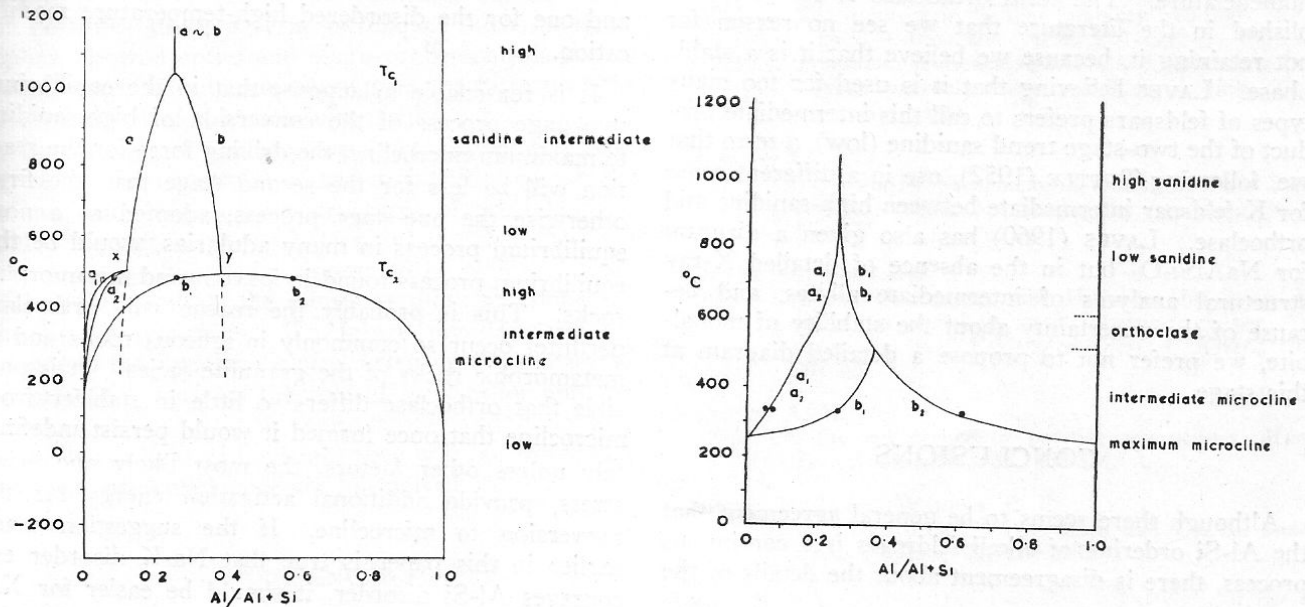
Fig. 5.—Suggested equilibrium variation with temperature of the distant Si, Al-O order of $KAlSi_3O_8$. Diagram 5 (a) is taken directly from LAVES (1960) and 5 (b) is the variation suggested by the present authors. The main differences between the two diagrams concern the nomenclature and the positions of the critical temperatures at which the ordering undergoes a discontinuity. The reasons for choosing the particular temperatures shown in 5 (b) are given in the adjacent paper by MACKENZIE and SMITH. The meaning of a_1, a_2, b_1, and b_2 is explained in the legend to Fig. 2.

After some changes of view, and of nomenclature, there is now good agreement between LAVES, GOLDSMITH and us on the role of orthoclase (or sanidine (low) in LAVES' nomenclature). It is regarded as having a field of stability at intermediate temperatures, and the observation that it does not give the "primitive" type of X-ray reflections is consistent with this view. The common occurrence of orthoclase perthites in slowly-cooled rocks suggests thaat there little difference in the free energy of orthoclase and microcline perthites and that it is difficult to overcome the energy barrier involved in the transformation between the two.

In the associated paper a possible phase diagram for alkali feldspars will be shown in the usual manner with temperature as ordinate and composition as abscissae. As four tetrahedra are involved the pattern of Al-Si ordering will be complex and LAVES (1960) has produced a useful diagram in which the ordering of a particular composition is plotted as a function of temperature. His diagram for K-feldspar is reproduced as Figure 5 a, and alongside it, our own version is reproduced as 5 b. These diagrams differ mainly in that LAVES assumes a critical temperature for completion of disorder whereas we put the critical temperature at the beginning of disorder. The reasons for using particular temperatures in our diagram are given in the adjacent paper. BAILEY's values of $Al/Al +$ Si for his intermediate microcline are used, and orthoclase in conformity with Fig. 1 is assumed to have values of 0.15 and 0.35 for its two types of tetrahedra. Another difference between the two diagrams is in the nomenclature. The term orthoclase is so well established in the literature that we see no reason for not retaining it, because we believe that it is a stable phase. LAVES believing that it is used for too many types of feldspars prefers to call this intermediate product of the two-stage trend sanidine (low), a term that we, following TUTTLE (1952), use in a different sense for K-feldspar intermediate between high-sanidine and orthoclase. LAVES (1960) has also given a diagram for NaAlSi$_3$O$_8$ but in the absence of detailed X-ray structural analyses of intermediate albites, and because of the uncertainty about the stability of monalbite, we prefer not to propose a detailed diagram at this stage.

CONCLUSIONS

Although there seems to be general agreement that the Al-Si ordering of alkali feldspars is a continuous process, there is disagreement about the details of the

process. McCONNELL and McKIE (1960), using the terminology of UBBELOHDE (1957), have suggested that the ordering of NaAlSi$_3$O$_8$ is a "smeared transformation", implying that there is "stable coexistence of two or more closely related structural modifications over a range of temperature", and that "in the temperature range of the smeared transformation the free energy must include terms arising from the strain and internal surface energy associated with domain boundaries" (9). While we agree that domains will be formed and that the free energy will contain terms arising from the strain and internal surface energy we believe that the situation is more complex and that it is an over-simplification to think of two different structural modifications. At any stage in the synthesis of albite the X-ray patterns are consistent with the presence of only one phase which varies in geometry as the synthesis proceeds. In the initial stages of ordering it seems best to regard the domains as fluctuations of order in a single lattice. But once these fluctuations have grown to produce anti-phase domains, the process of ordering will involve merely an increase of the perfection of order in the domains — and only *one type of structural modification* will be involved (of course, there will still be fluctuations of order). A process that does appear to be a smeared transformation is the non-equilibrium transformation of low albite to high albite by heating at 1050°C., and the similar transformation of microcline to sanidine (GOLDSMITH and LAVES, 1954 b) in which the X-ray patterns show two sets of reflections, one for the low-temperature form and one for the disordered high-temperature modification.

It is reasonable to suppose that in the equilibrium two-stage process of the conversion of high-sanidine to maximum microcline, the driving force for the reaction will be less for the second stage than the first, otherwise the one-stage process, adopted as a non-equilibrium process in many adularias, would be the equilibrium process found in igneous and metamorphic rocks. This is probably the reason why orthoclase perthites occur so commonly in igneous rocks and in metamorphic rocks of the granulite facies. It is possible that orthoclase differs so little in stability from microcline that once formed it would persist indefinitely unless other factors, the most likely one being stress, provide additional activation energy for the conversion to microcline. If the suggestion made earlier in this paper is true that Na-K disorder encourages Al-Si disorder, it should be easier for Na-free K-feldspars to convert into microcline than igneous ones which would have to start from an orthoclase or a sanidine containing at least 10-20 per cent

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point out that orthoclase cannot be the form of K-feldspar stable at absolute zero because disorder cannot occur at absolute zero. As described earlier, all evidence suggests that maximum microcline is either fully ordered or nearly fully-ordered and consequently from a thermodynamic viewpoint could be the form stable at low temperatures.

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(9) Quotations are from UBBELOHDE's paper.

of Na in substitutional disorder. Consequently authigenic microclines should be able to form at a higher temperature than igneous equivalents, or to put it another way, should be able to form more easily at a given temperature than their igneous equivalents.

The domain structure in microclines, when developed on a coarse enough scale, reveals itself as albite and pericline twinning. Domain structure produced during the formation of orthoclase from high sanidine cannot reveal itself optically as twinning because of the lattice constraints enforced by the monoclinic symmetry. Consequently a study of this domain structure must be made by X-ray methods. The presence of diffuse reflections mentioned earlier, shows that such domains exist, but our knowledge of them must remain incomplete until these diffuse reflections have been accurately measured and interpreted.

Although a large body of optical evidence on the perthitic structure has been gathered (for example, ANDERSEN, 1928, SPENCER, 1937, among many other papers) it seems probable that the situation is much more complex than has been described. For as the Si and Al atoms become more ordered, the two components of the perthite will become purer and movement of Na and K atoms will take place. It is not necessary that the released atoms move through the lattice to join up with a feldspar component that is primarily composed of similar atoms: they may form new perthite units. SPENCER has described the presence of both shadow perthite and microperthite in a number of feldspars and this may result from two different periods of exsolution. Further careful study of perthites using several techniques such as light-optics, electron optics and micro-probe analysis should reveal much information bearing on the history of the feldspars and of the containing rocks.

In this review article, we have deliberately laid stress on the uncertainties and ambiguities remaining in our knowledge of the structures of the feldspars, and consequently we wish to point out that the keystones of our knowledge appear to be well and truly laid as the result of the efforts of those mentioned in the list of references. To future investigators, we commend the importance of clearing up the remaining uncertainties, such as the role of local order and the variation of order with temperature, and hope that in the harsh light of hindsight they will not think that the ideas presented here are too naive!

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DISCUSSION

MEGAW (Cambridge):

1. I agree with Dr. SMITH in distinguishing between the effects of what he calls «long-range» and «short-range» order, but I would like to ask him to use different names, for example «extensive order» or «average order» and «local order». The «long-range order parameter», as defined by Bragg for the alloys, is *zero* if there are antiphase boundaries, and I do not think this is a useful definition for silicates. Similarly the «short-range order parameter», defined from the work of Bethe on alloys, depends on interchanges between neighbouring atoms, and cannot be transferred to the silicates without making confusion.

2. I think that there are in fact three kinds of disorder to be considered: (a) antiphase boundaries extending as infinite sheets (perhaps intersecting one another), (b) closed-circuit interchanges, (c) random replacement. Which happens in which feldspar we do not yet know, but this kind of distinction will be needed to discuss details as new work appears.

3. To the kinds of phase trasition I would add mention of the *displacive transitions* distinguished by Buerger. These involve *no* interchange of atoms, but a distortion or straightening out of the framework, and happen reversibly in a single crystal. There are increasing numbers being reported, including many in ferroelectric materials; but conventional thermodynamics has not taken account of them. I believe that such transitions occur in feldspars, and underlie all the ordering processes. I shall be developing this idea in my final paper.

J. V. SMITH (Chicago):

Answer to (1): This is a good suggestion and we have no objection to using terms such as «local» and «distant» order. — Answer to (3): We are well aware of the elegant work of Buerger on displacive and reconstructive transformations. Also we are aware of work going on at the present time on these transitions that show they are more complex than Buerger described; in particular, displacive inversions such as the high-low quartz change have been found to show a forewarning.

LAVES (Zurich), comments on Megaw's discussion:

To 1. As to the question of the desirability of introducing new words in addition to «long-range» and «short-range» order (Fern- und Nah-Ordnung) I doubt the necessity at this stage as long as not discriminating definitions are given. It is true, Bethe's original definition for short range order applies to a relatively simple model in which only *one* short range order parameter is needed. Bethe's concept could be amended, however, to fit more complex systems by using more parameters, be it to treat alloys or silicates (i.e. in the alkali feldspars three parameters would be needed to characterize the Al/Si distribution; whereas Bethe considers interchanges between neihgbouring atoms, interchanges between Al and Si in neighbouring (Al, Si) O₄-tetrahedra have to be considered in feldspars). There appears to be no basic difference between alloys and silicates in the description of order/disorder relations from a geometrical point of view. However, it might be desirable and very valuable to introduce a new term

like «local» order if domains are meant which developed either as nuclei or as relics and which have a higher (or less) degree of short range order than the surrounding material, i.e. if there are fluctuations which are considered as exceeding those to be expected under equilibrium conditions and which appear as domains that have a degree of short range order different from the degree of short range order of the surrounding matrix.

To 3. 1952 (J. Geology 60 p. 436-450) the importance of the concept of the displacive transformation was discussed in interpreting the analbite-monalbite (at that time called barbierite) transition. It is now no longer a matter of belief but of fact, that displacive transformations *and* diffusive transformations (the latter term introduced in 1952) play an important role in the understanding of the feldspar relations. The reader is referred to a further discussion on this point by LAVES and GOLDSMITH (this volume) in their «Comments on the anorthite papers by Megaw and coworkers».

LAVES (Zürich):

1. The present writer disagrees somewhat with the concept that the K/Na ratio has such a great influence on the Al/Si-distribution in the feldspars as proposed by the authors. Reasons for this disagreement are given in the discussion on the following paper by MACKENZIE and SMITH (point A, 2; E and F).

2. To clear up differences of opinion on the use of the word «orthoclase» (having «monoclinic symmetry» on page 41 of the paper, but showing indications of triclinic domain-twinning on page 49 of the paper) the reader is referred to discussions on the following paper (point C). It is interesting, however, to note here that the «orthoclase» concept developed by LAVES (1950, 1952), GOLDSMITH and LAVES (1954), LAVES (1960) and by LAVES and GOLDSMITH (this symposium) is very nicely summarized by SMITH and MACKENZIE on page 46. At least, it is now agreed that such material must exist. However, no name is proposed by SMITH and MACKENZIE to distinguish such material from that which is called orthoclase in the preceding paper and in the following one by MACKENZIE and SMITH.

3. With respect to «pericline» mentioned by the authors on p. 43, the present writer doubts in part the proposed analogy to adularia, because evidence was given by LAVES and SCHNEIDER (1956) that «pericline» is a product of replacement in crystals originally grown as plagioclase with some oligoclase composition. This viewpoint could be supported by additional observations (a paper on this problem is in preparation), which clearly show that this replacement is a discontinuous process leading to oligoclase and albite in close coexistence (not necessarily considered to be a stable one).

4. It is gratifying to note that SMITH and MACKENZIE agree (p. 46) with the point of view taken by the writer since 1952 (p. 558, 5. and p. 567, 4.), that the difference of the compositions between two perthitic components will be determined by the particular state of Si-Al order achieved by the feldspar. (Compare in this connection the remark by the present writer on the following paper by MACKENZIE and SMITH, Comment D, p. 66.)

5. On page 46 SMITH and MACKENZIE propose *discontinuous* transitions for K and Ca containing Na-rich feldspars. The writer did and does not believe in discontinuities unless unmixing processes are meant to produce coexisting feldspars of different composition (for example peristerite-type unmixing).

6. On page 48 SMITH and MACKENZIE mention an «uncertainty about the stability of monalbite», on the other hand MACKENZIE and SMITH (this volume) admit the stable existence of a truly monoclinic modification of $NaAlSi_3O_8$, above approximately 950° C. The writer is somewhat confused! — Since the heating experiments of BASKIN (1956) and SCHNEIDER (1957) who produced ideal microcline-twinning of acid plagioclases there should be no doubt any more about the fact *that monoclinic $NaAlSi_3O_8$ has a stability field* at temperatures near the melting point. It is true, MACKENZIE (1952) published data for powders X-rayed at high temperatures indicating strongly the existence of monoclinic symmetry at high temperature. On the other hand, the writer has some doubts (discussed 1960, p. 283, 285) on the validity of those extrapolations which led MACKENZIE (1952) to propose that there are «albites» which should convert to monoclinic symmetry at temperatures higher than the melting point on superheating (non-equilibrium conditions).

7. In connection with the remarks on perthites on the end of the paper it may be permitted to add here some observations (to be published soon jointly with K. Soldatos). Many microcline perthites have been investigated by X-ray methods to reveal the orientation relations which exist between the microcline and the albite. Several modes of orientation relations have been found which indicate that most of the $NaAlSi_3O_8$ has been exsolved when the morphological units were still «monoclinic». This holds for the coarse «vein-perthite» and those micro-perthites which may correspond to ANDERSEN's (1928) «film»- and «string»-perthites (plus crypto-perthite in many cases), indicating predominantly two generations due to unmixing from truly monoclinic sanidine on the one hand and from states which are considered to be «orthoclase» [in the sense defined by LAVES (1952) and by GOLDSMITH and LAVES (1954)] or very finely twinned microcline on the other hand. In addition a third generation of cryptoperthites was found that has been exsolved after a considerable enlargement of the microcline twin-domains took place due to a process of «secondary recrystallization». In microcline units that might be considered to have progressed very far in recrystallization (nearly and virtually «single crystals») one more kind of perthitic intergrowth was found. It is developed as a «microperthite» distinguished from the types mentioned before by the following features: The albite is oriented by a characteristic albite/microcline orientation relation in such a way that «coherency» between the microcline and albite structures exists as far the topological Al/Si-distribution in the two $AlSi_3O_8$-frameworks is concerned.

J. V. SMITH (Chicago) and MACKENZIE (Manchester). Answer:

1. See reply to 4.

2. LAVES implies that there is something incompatible with orthoclase having monoclinic optical symmetry on page 41 and showing indications of triclinic domain twinning on page 49. Actually these are compatible because the domain structure that is revealed by X-rays can be on too fine a scale to be resolved by optical methods and consequently the optical symmetry is monoclinic. To the best of our knowledge there has never been disagreement that orthoclase is partly ordered (for example, CHAO, HARGREAVES and TAYLOR proposed this in 1940 and obtained some experimental evidence in support of the idea). LAVES has focused attention onto the domain structure and we have emphasized the overall monoclinic geometry. Actually both concepts are compatible because the local symmetry in a domain will be triclinic but the overall statistical symmetry will be mono-

clinic. Consequently, there neither has been nor is disagreement on the nature of orthoclase but there has been a difference in emphasis. LAVES says that we propose no name to distinguish this material from that described in the preceding and the following paper by MACKENZIE and SMITH (this volume). Presumably this latter material is natural orthoclase. If so, we do not propose a new name for we use orthoclase both for the natural specimens and for the theoretical partly-ordered K-feldspar. The reason is that we believe that the natural specimens have essentially the same Al-Si order as the theoretical feldspar, and because we rely on the context of the term to indicate whether we are talking about the natural specimens or the theoretical structure type. Consequently LAVES' theoretical sanidine (low) is the same as our orthoclase used in a theoretical context.

3. This is a good point. However we wonder if all albites of the pericline or authigenic type have formed by ion exchange from oligoclase. We suspect that some have formed directly as pure albite, and have followed a non-equilibrium path such as that of adularia. Further investigation of these types of specimens would be desirable.

4. In equilibrium we believe that the composition and Al-Si order are interrelated so that they are interdependent. We believe it is an over-simplification to consider that one controls the other, though they will affect each other. Disorder in one set of atoms should encourage disorder in the other set.

5. We are forced to propose a discontinuous transition in Ca-bearing alkali feldspars because TUTTLE and KEITH (1954) and EMELEUS and SMITH (1959) have observed perthites from granites and porphyries that contained both anorthoclase [about Or_{80} $(Ab + An)_{20}$] and albite-oligoclase (about An_5-An_{30}) together with a K-feldspar. Whether the sharp change in composition occurs under equilibrium conditions is not known. In pyroxenes a discontinuous composition change (POLDERVAART and HESS, 1951) has been proposed between augite-pigeonite and augite-hypersthene intergrowths. We see no theoretical reason why a discontinuous change should not occur in these Ca-bearing feldspars. It should be noted that we have not proposed a discontinuous change in Ca-free alkali feldspars.

6. We are seriously concerned about the extent of the stability field of monalbite. A common criterion of stability is reversibility of reaction, though this is not a sufficient condition. Until the reactions obtained in albite by heating just under the melting point are reversed by heating at lower temperatures, we think that the onus is on LAVES to demonstrate the stability of the types of albite made by him and his co-workers. Furthermore we think that the formation of a glass shell on the crystal used by BROWN suggests partial melting or loss of material by volatilization. Again, we would like to see experiments in which no glass was produced.

7. These new data are welcomed in providing yet further evidence of the complexities of the order-disorder and unmixing processes.

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Experimental and geological evidence for the stability of alkali feldspars [1]

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ABSTRACT.

The experimental evidence for establishing the relative stabilities of the various forms of the alkali feldspars is as yet incomplete. The observations of geological occurrence taken together with the results of hydrothermal and dry-heating studies of natural and synthetic feldspars make it possible to construct a phase diagram showing the probable equilibrium relations.

Since petrological theories are frequently based on the type of potassium feldspar present in a rock, the question of the relative stabilities of orthoclase and microcline is discussed in detail.

INTRODUCTION

The relationships between the various forms of potassium feldspar have been the object of researches by petrologists, mineralogists and crystallographers for many years and may be said to date back to the publication of Mallard's hypothesis in 1876. In the case of sodium feldspar, however, it was not until the publication of the Feldspar Issue of the *Journal of Geology* in 1950 that it was clearly established by Tuttle and Bowen that more than one form of albite exists, although a number of previous studies had indicated that there might be a form other than the common form found in pegmatites and granites. In the same issue of that Journal an accompanying paper by Bowen and Tuttle described the experimental determination of the alkali feldspar solvus and Laves (1950) published the results of an X-ray study of the lattice and twinning of potassium feldspars. The great interest in the feldspars which has been apparent in the last decade undoubtedly stems from these publications.

Most petrologists have assumed that the form of potassium feldspar stable at low temperatures is microcline and that orthoclase is stable at somewhat higher temperatures. There have been two noteworthy exceptions, however, one of them based on observations of natural occurrences of the minerals (Eskola, 1951), and the other based on a hypothesis that charge balance controls the stability of the feldspars (Ferguson, Traill and Taylor, 1958; Ferguson, 1960). Another completely different view is that of

Laves (1952) who has considered orthoclase to be a metastable form of potassium feldspar.

Since much of the theory on which the science of petrology is founded is based on a knowledge of the relative stabilities of minerals it is important that the information available on the common rock-forming minerals should be as accurate as possible. It is therefore with no apology that we survey again some of the available evidence as to the relative stabilities of the feldspars and the possible applications of the information to the study of natural rocks.

Since neither low temperature albite nor microcline has yet been synthesised from a mixture of oxides or from a glass of the required composition, most of the information available on the stability of the low-temperature forms is based on the results of study of the natural occurrences of the minerals and the effect of heating the minerals under a variety of conditions. In the study of natural minerals the likelihood of a close approach to equilibrium conditions in geological time is outweighed by the great disadvantage that the interpretation of the conditions of formation may be liable to many uncertainties. Experimental studies have the advantage of controlled conditions of synthesis and a relatively easy interpretation of the results but, certainly in the case of the feldspars, it appears that the approach to equilibrium is a very slow process and may not be achieved in the short time available in the laboratory.

SODIUM FELDSPAR

Tuttle and Bowen (1950) from a study of synthetic feldspars of albite composition and the effect of

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prolonged heat-treatment of low temperature albites, established conclusively the existence of a high-temperature form of $NaAlSi_3O_8$: no intermediate forms were found and they concluded that the inversion temperature from the low to the high form was probably not above 700°C. MacKenzie (1957) showed that albites with lattice parameters intermediate between those of high- and low-albite could be synthesised in the presence of water vapour under pressure in experiments of long duration: since the lattice parameters of the albites, crystallized for long periods at constant temperature, tended to equilibrium values it was suggested that for each temperature there was a stable form of $NaAlSi_3O_8$, low-albite being stable only below about 450°C. McConnel and MacKie (1960) made a kinetic analysis of MacKenzie's experimental data and from this have postulated the existence at 575°C. ± 25°C. of a "smeared thermal transformation".

MacKenzie (1952 b) showed that a monoclinic form of $NaAlSi_3O_8$ could exist at high temperatures when a synthetic albite crystallized above about 950°C. was heated: on cooling the symmetry reverted to triclinic. Feldspars of albite composition when crystallized below about 950°C. do not acquire monoclinic symmetry on heating up to the melting point. In 1957 MacKenzie assumed that since only specimens crystallized above about 950°C. acquire monoclinic symmetry it is likely that the materials used in 1952 were the stable forms for the temperature of crystallization so that a monoclinic form of $NaAlSi_3O_8$ is only stable above about 950°C. and cannot be expected to occur in rocks because the monoclinic-triclinic inversion is non-quenchable. Brown (1960) has, however, shown by prolonged heating of a natural albite at a temperature close to the melting point, and subsequent rapid cooling, that the temperature of the monoclinic-triclinic inversion is gradually lowered by continued heat treatment until a stage is reached when a monoclinic form of $NaAlSi_3O_8$ may exist at room temperature. The specimen of natural albite investigated by Brown (1960) had been previously heated by Schneider (1957) for 70 days at 1000°C. by which time it had acquired lattice parameters appropriate for high-albite, viz:

$$\alpha^* = 86° \ 15'; \ \gamma^* = 88° \ 06' \text{ and } a^* = 0.1370 \ (\text{Å}^{-1});$$

compare the values for high-albite given by Smith, J. V. (1956):

$$\alpha^* = 86° \ 0'; \ \gamma^* = 88° \ 0' \text{ and } a^* = 0.1368 \ (\text{Å}^{-1}).$$

Thereafter Brown heated the specimen for 20 days at 1050°C. and its parameters changed significantly; after a total of 35 days at 1050°C. it remained monoclinic in symmetry when observed at room temperature.

Baskin (1956 b) heated specimens of authigenic albite at about 1120°C. for up to 29 days and measured the lattice constants at frequent intervals. After 10 days at 1120°C. the transformation to high albite was completed and the additional 19 days produced no significant changes in any of the lattice dimensions. Baskin reported that after a month at about 1120°C. the authigenic albite crystal melted. There is some discrepancy between these results and those obtained by Brown since the higher temperature used by Baskin would be expected to promote further changes in the high albite more readily than heating at 1050°C.

J. R. Smith (1958) heated a specimen of the albite from Ramona, California ($Or_{1.2}Ab_{98.6}An_{0.2}$ wt. %) for 24 ½ days at 1080°C. and by measurement from an X-ray powder diffraction pattern ($CuK\alpha$) obtained a value for $2\theta \ (131) — 2\theta \ (1\bar{3}1)$ of 1.98° which is consistent with that of high temperature albite. Although both Brown and Smith (J. R.) mention the presence of some glass in heated feldspar samples, Smith states that the glass he saw is related to the presence of inclusions and in the specimen of Ramona albite, which contained very few inclusions, there was "very little glass after heating". Brown states that a film glass "develops on albite crystals when heated for long periods of time at 1050°C.".

It would be invalid to make a direct comparison between these three studies since different materials were used and the temperatures of heating were different. However, since Brown used the lowest temperature it is rather surprising that he obtained a film of glass on his crystals and that after only 20 days at 1050°C. the lattice parameters had changed from those of high-albite. It would be most instructive to determine whether the change discovered by Brown can be reversed. At the present stage we prefer to reserve judgement on the stability of a form of albite which is monoclinic at room temperature although there would appear to be general agreement that above about 950°C. albite may exist in a monoclinic form.

Laves (1960) has recently discussed the stabilities of the forms of $NaAlSi_3O_8$ and considers that there are two stable forms, viz: monalbite which is truly monoclinic and albite which is truly triclinic. Each of these he considers may be divided into high, intermediate and low forms depending on the degree of Al/Si order present. The form which he has called analbite he considers to be metastable and is defined as a form characterized by triclinic symmetry with an Al/Si distribution which allows it to become monoclinic on heating without noticeable change in the Al/Si distribution. Albite on the other hand tends towards monoclinic symmetry with rising temperature with a change in the Al/Si distribution. The experimental study of MacKenzie (1957) on the synthesis of $NaAlSi_3O_8$ at different temperatures and times is relevant to this discussion. It was noted by MacKenzie that from a glass of albite composition a great

variety of different forms of $NaAlSi_3O_8$ could be produced. Using the value of $2\theta_{131} - 2\theta_{1\bar{3}1}$ measured from powder diffraction patterns to characterize the forms of albite, it was found that a number of different forms having the same value of $2\theta_{131} - 2\theta_{1\bar{3}1}$ could be synthesised: these findings may be related to the proposals put forward by LAVES. Thus the high, intermediate and low forms of albite which MACKENZIE considered to be stable forms may be equated with the albite (high), albite (intermediate) and albite (low) of LAVES and the forms which MACKENZIE considered

A number of workers have conducted experiments on prolonged heating of low temperature albites at temperatures close to the melting point and have obtained different results by using different specimens of albite. TUTTLE and BOWEN (1950) noted that whereas Amelia albite could be converted to the high-temperature form on heating at 1050°C. for 10 days, Varuträsk albite was only partially changed to the high form in three weeks and an albite from Avondale, Pennsylvania, was changed very little in that time. J. R. SMITH (personal comunication) made a study
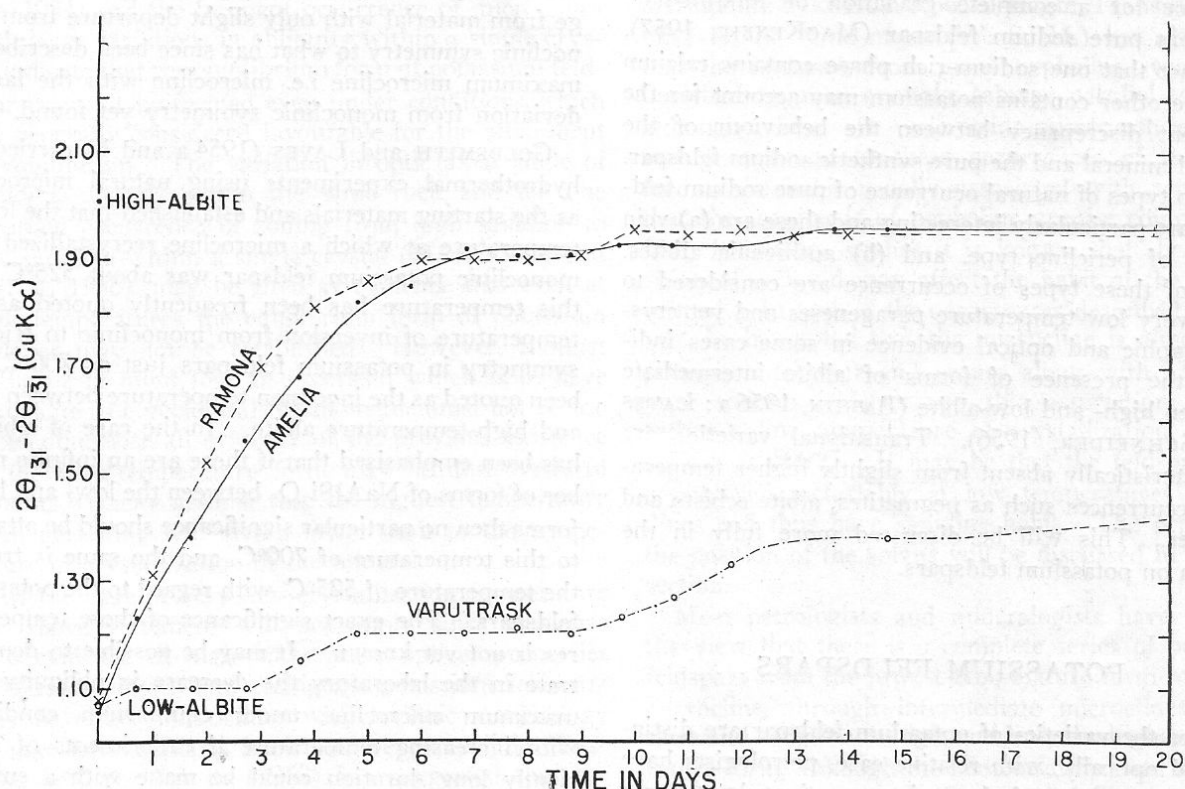
Fig. 1.—Diagram showing the rate of change in $2\theta_{131}-2\theta_{1\bar{3}1}$ ($CuK\alpha$) of three specimens of low-albite heated at 1080°C. Unpublished data of Dr. J. R. SMITH reproduced with his permission.

metastable may correspond to those which LAVES has now designated analbites (1).

There are still large gaps in our knowledge of the varieties of forms of $NaAlSi_3O_8$ as can be seen from the foregoing discussion and it may be argued that the natural minerals, when nearly pure $NaAlSi_3O_8$, are generally in the low temperature form so that further detailed study of the possible varieties of sodium feldspar is of very limited value for the geologist. However, this may not be entirely true as will be shown below.

of the rates of transformation to the high-temperature form of three analysed samples of low-albite and Fig. 1 is reproduced with Dr. J. R. SMITH's kind permission. These differences in response to heat treatment might be attributed to slight differences in chemical composition of the materials but it is much more likely to be due to different crystallization histories. This conclusion is supported by the results of both hydrothermal and dry heat treatment of synthetic albites crystallized at different temperatures (MACKENZIE, 1957).

If the differences between the high and low forms of albite are mainly due to the Al/Si distribution there must be a number of paths by which the fully ordered low form is reached, as GOLDSMITH and LAVES

(1) In this recent paper LAVES (1960) has redefined his usage of the term analbite so that it no longer corresponds to the form described by TUTTLE and BOWEN (1950) as high-albite.

(1954 b) have proposed for the potassium feldspars. If the nature of the differences between different specimens of low albite can be related to crystallization temperature a significant contribution to petrology would result.

Very little information regarding the stabilities of the different forms of albite has been obtained from the study of natural ocurrences chiefly because of chemical variations in the high forms. The coexistence of two sodium-rich phases in some microperthites (MACKENZIE and SMITH, 1956) is in conflict with the evidence for a complete gradation of intermediate forms in pure sodium feldspar (MACKENZIE, 1957). The fact that one sodium-rich phase contains calcium and the other contains potassium may account for the apparent discrepancy between the behaviour of the natural mineral and the pure synthetic sodium feldspar.

Two types of natural ocurrence of pure sodium feldspars are particularly interesting and these are (a) vein albites of pericline type, and (b) authigenic albites. Both of these types of occurrence are considered to be of very low temperature parageneses and yet crystallographic and optical evidence in some cases indicates the presence of forms of albite intermediate between high- and low-albite (BASKIN, 1956 a; LAVES and SCHNEIDER, 1956). Transitional varieties are characteristically absent from slightly higher temperature occurrences such as pegmatites, albite schists and granites. This will be discussed more fully in the section on potassium feldspars.

POTASSIUM FELDSPARS

Since the varieties of potassium feldspar are distinguished optically, with relative ease, petrologists have long been aware of the existence of at least three "polymorphic" forms of potassium feldspar and have attempted to determine their relative stabilities both from their geological occurrence and from studies of the effects of heat treatment on the natural minerals. Experimental studies have been hindered by the failure to synthesise directly, from a mixture of oxides or from a glass, any form other than the highest temperature form, viz: high sanidine. A brief review of some of the more recent experimental studies of the potassium feldspars follows.

It has been generally recognized that heat treatment of all forms of potassium feldspar at a temperature fairly near to the incongruent melting temperature produces a form which was designated by TUTTLE (1952) as high-sanidine, i.e. a monoclinic feldspar with the optic plane parallel to (010) and having an optic angle of about 50-60° (the size of the optic angle depending on the composition of the feldspar). Some feldspars

are much more difficult to convert to the high sanidine form than others. In 1950 LAVES made a significant contribution to our knowledge of the potassium feldspars by showing that microclines, which have the characteristic cross-hatched twinning, undoubtedly crystallized with monoclinic symmetry and subsequently inverted to triclinic symmetry. Although the first measurements (Laves, 1950) showed two sets of angles for triclinic K-feldspars, it was soon established by both MACKENZIE (1952a, 1954) and by LAVES and GOLDSMITH (LAVES, 1952; GOLDSMITH and LAVES, 1954a, b) that triclinic K-feldspars cover a whole range from material with only slight departure from monoclinic symmetry to what has since been described as maximum microcline i.e. microcline with the largest deviation from monoclinic symmetry yet found.

GOLDSMITH and LAVES (1954 a and b) carried out hydrothermal experiments using natural microclines as the starting materials and established that the lowest temperature at which a microcline recrystallized to a monoclinic potassium feldspar was about 525°C. and this temperature has been frequently quoted as the temperature of inversion from monoclinic to triclinic symmetry in potassium feldspars just as 700°C. has been quoted as the inversion temperature between low- and high-temperature albite. In the case of albite it has been emphasised that if there are an infinite number of forms of $NaAlSi_3O_8$ between the low- and high-forms then no particular significance should be attached to this temperature of 700°C. and the same is true of the temperature of 525°C. with regard to the potassium feldspars. The exact significance of these temperatures is not yet known. It may be possible to demonstrate in the laboratory the decrease in obliquity of a maximum microcline under equilibrium conditions with increasing temperature if experiments of sufficiently long duration could be made with a suitable catalyst such as water vapour under pressure: if it can be shown that a microcline with small obliquity acquires monoclinic symmetry at just above 500°C. and the process can be reversed just below 500°C. then it can be stated that the temperature of the symmetry change is 500°C.

It is clear from the heating experiments on microclines carried out by many workers that the obliquity of a microcline may be independent of the chemical composition of the crystal. This does not exclude the possible rôle of the sodium content and perhaps even the small calcium content of a microcline in having some influence on the obliquity. It is undeniable that distribution; but only in the case of a pure potasium the main factor in controlling the obliquity is the Si/Al distribution; but only in the case of a pure potassium feldspar can this be completely divorced from the Na/K ordering process; this is discussed more fully below.

Although it is suggested that the different forms of potassium feldspar, as defined by TUTTLE's curves of optic axial angle against chemical composition, each have a range of temperature of stability, it is not yet possible to assign with any degree of certainty temperature ranges to these forms. TUTTLE and BOWEN (1958) have tentatively placed the change from low to high sanidine at 800°C. on the basis of SPENCER's (1937) heating experiments, and the change from orthoclase to sanidine they have placed at about 650°C. The occurrence of a monoclinic feldspar and a microcline of high obliquity in the same crystal (MACKENZIE, 1954) and the frequent occurrence of microclines with large variations in obliquity within a single crystal indicate that the equilibrium form of potassium feldspar may not be formed even under conditions which are generally considered favourable for the attainment of equilibrium. The variation in optic axial angle of sanidine crystals within the same rock and the one recorded occurrence of zoning from high sanidine to low sanidine within a single crystal (MACKENZIE and SMITH, 1956), may be cited as evidence that even at high temperatures the equilibrium form of potassium feldspar may not be established. However, it must be borne in mind that an inversion which is to have any value as a geological thermometer must not be too rapid otherwise all evidence of the previous existence of the high-temperature form may be destroyed: in general we may assume that the highest temperature form persisting will give a lower limit to the temperature of crystallization of the mineral.

In the case of very low crystallization temperature the above statement will not apply since adularias give evidence of high-temperature optical properties (CHAISSON, 1950) and authigenic potassium feldspars may be either microclines with triclinic morphology or may have adularia habit and be monoclinic (BASKIN, 1956 a). LAVES (1952) has suggested that the rate of growth of adularia may be suffiently high that the ordering forces are overwhelmed during crystallization, producing a more or less disordered framework. GOLDSMITH (1953) has discussed the strong tendency for potassium feldspars to crystallize metastably as the disordered modification and hydrothermal syntheses of both the sodium and potassium feldspars point to the same conclusion. Those authigenic feldspars which have triclinic morphology presumably have crystallized much more slowly than adularias and it may be assumed that those which are maximum microclines have crystallized more slowly than those which are intermediate microclines. The alternative possibility is that both the maximum and intermediate microclines crystallized as the stable forms, the intermediate microclines crystallizing at a higher temperature than the maximum microclines: this requires that the upper stability limit of maximum microcline should be at a temperature of perhaps 200°C. or even less.

BARTH (1959) has recently proposed that disorder becomes apparent in potassium feldspar above about 300°C. The concept of metastable formation of high temperature forms at low temperatures introduces a further complexity in the interpretation of the stability of the feldspar from natural occurrences.

One observation which is of interest in a consideration of the stability of potassium feldspars is the occurrence of microclines with tabular habit after {010}, a habit which is characteristic of sanidines. TILLEY (1956) has noted this feature in a foyaite from the Pilansberg and again in the pegmatitic facies of a mariupolite dyke from Koedoeslaagte, Transvaal (TILLEY, 1960). One of us (W. S. M.) has also noted that the feldspars from many nepheline syenites are Carlsbad twinned crystals, tabular parallel to {010} although they are microcline-microperthites. The feature common to these occurrences of microcline having the habit usually associated with sanidine is that the magma is of nepheline syenite composition; from laboratory studies it is known that the composition of a liquid may affect the habit of the crystals formed. In both of the occurrences described by TILLEY, he has noted that the microcline is almost pure potassium feldspar and occurs along with an almost pure sodium feldspar and this association requires rather a low temperature of crystallization, perhaps as low as 500°C. It may be that the feldspars have crystallized metastably at low temperatures as sanidines and thus have sanidine habit. The problem of the position of the solvus will be discussed in the next section.

Most petrologists and mineralogists have accepted the view that there is a complete series of potassium feldspars from the lowest temperature form maximum microcline, through intermediate microclines, orthoclase and sanidine to high sanidine, the highest temperature form, although the nomenclature used may vary somewhat. FERGUSON, TRAILL and TAYLOR (1958), however, have proposed a new hypothesis that electrostatic neutrality of a feldspar can be equated with stability and have concluded that the stable form of potassium feldspar is monoclinic in symmetry and they have described this form as "ideal orthoclase". In order to explain the common occurrence of microcline instead of orthoclase these authors have proposed an exsolution theory for the origin of microcline in which it is suggested that the nature of the Al/Si framework of the low temperature mineral is controlled by the proportion of Na to K in the high temperature form which crystallized originally. This theory has recently been expanded by FERGUSON (1960) who has suggested that the intermediate microcline whose structure was accurately determined by BAILEY and TAILOR (1955) was derived by unmixing from a crystal of composition near $Or_{50}Ab_{50}$ although the actual microcline-cryptoperthite studied has a compo-

sition of $Or_{85.9}Ab_{12.7}An_{1.4}$ (weight %). FERGUSON (1960) points out that no correlation is necessarily to be expected between the sodium content of a particular mineral and its lattice geometry since some of the sodium may have migrated outside the boundaries of the original crystal (see TUTTLE, 1952). However, there should be a correlation between the total sodium feldspar content of a rock and the type of potassium feldspar and no such correlation can be found on examining descriptions of such rocks as mariupolites compared with juvet-type nepheline syenites or descriptions of sodium-rich granites compared with potassium-rich granites.

At the other extreme is the viewpoint of LAVES who has several times cast doubt on the stability of natural orthoclase, because of the slightly variable X-ray properties. MACKENZIE and SMITH have been more optimistic in thinking that the orthoclase from many granites —defined on the 2V versus composition of TUTTLE (1952)— is a stable form at some intermediate temperature, or at least is quite close in structure to a stable intermediate form. Believing that orthoclase differs somewhat from the stable intermediate forms, LAVES (1960) uses the term sanidine for all monoclinic K-feldspars, and microcline for all triclinic varieties. He subdivides sanidine into sanidine (high), sanidine (intermediate) and sanidine (low) and he has given these terms a theoretical explanation in terms of Al-Si ordering. For naturally- occurring feldspars he uses the terms sanidine, adularia and common orthoclase, the latter of which he regards as beeing rather imprecise, covering a variety of different states. Because MACKENZIE and SMITH believe that the natural orthoclase from igneous rocks, that has the optical properties defined by TUTTLE's 1952 data, corresponds closely to a stable intermediate K-feldspar, they use the term orthoclase (1) both for naturally-occurring specimens and for the theoretical concept of sanidine (low) created by LAVES. This practice ought not to lead to confusion because the context shows in which sense the word orthoclase is used. Furthermore, it is thought that this makes it easier for non-specialists to follow the development of current feldspar research.

The observation that diffuse streaks occur in X-ray patterns of orthoclase (LAVES, 1950) is not regarded as satisfactory evidence that orthoclase cannot be stable at any intermediate temperature. The diffuse streaks are thought to arise from fluctuations of Al-Si order that will occur in all feldspars with partial ordering whether stable or metastable.

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(1) Homogeneous orthoclases near to pure potassium feldspar in composition are comparatively rare as also are nearly pure potassium-sanidines ; the liquids from which they crystallize probably have considerable amounts of sodium present and thus control the composition of the crystals.

THE ALKALI FELDSPAR SOLVUS

Since it has been suggested that the ordering of the Na and K atoms and the ordering of the Al and Si atoms are closely related, a consideration of the experimental studies of the alkali feldspar solvus may provide information about the relationship between these two processes.

TUTTLE and BOWEN (1958) published data on three solvi, one determined using synthetic feldspars, one using natural sanidine-cryptoperthites and one using natural orthoclase-microperthites: their diagram is reproduced as figure 2. The crest of the solvus for natural sanidine-cryptoperthites is about 100°C. lower
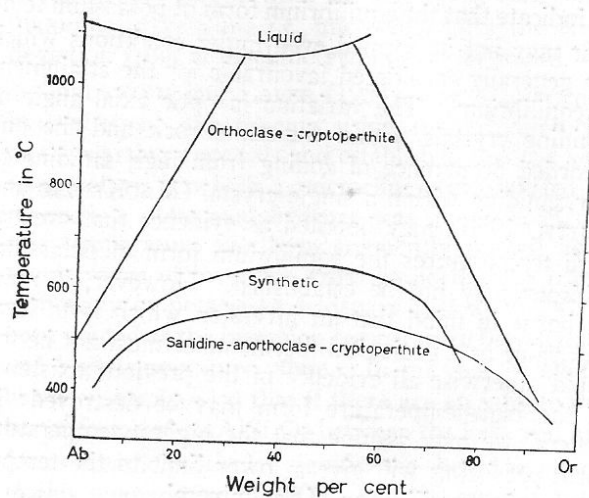
Fig. 2.—Three alkali feldspar solvi determined by using: (a) orthoclase-microperthites, (b) synthetic feldspars, (c) sanidine- and anorthoclase-cryptoperthites. (After TUTTLE and BOWEN, 1958.)

than that for the synthetic feldspars. It has been shown experimentally that the effect of calcium is to raise the solvus until it eventually intersects the liquidus surface: it must then be explained why the solvus for the natural high-temperature feldspars, all of which contain some calcium, is lower than that for the calcium-free synthetic feldspars. TUTTLE and BOWEN (1958) established by three separate methods that they had determined the equilibrium solvus for the synthetic feldspars but this does not necessarily mean that the synthetic feldspars were the stable forms in the temperature range in which they were working. It is believed that the differences in the three solvi are due to the different degrees of Al/Si ordering in the three types of feldspars and having decided which is the stable solvus something can be said about the degree of Al/Si ordering at the crest of the solvus.

It was suggested by SMITH and MACKENZIE (1958) that natural sanidine-cryptoperthites were more likely to have the appropriate amount of Al/Si ordering in the temperature range of the top of the solvus than

were the rapidly crystallized synthetic feldspars. This view we have now revised since a redetermination of the sodium-rich limb of the solvus by SMITH and MAC-KENZIE using a sanidine-cryptoperthite showed about 25 % of potassium feldspar in solid solution in albite at 450°C. and MACKENZIE's (1957) study of the forms of $NaAlSi_3O_8$ indicated that low temperature albite was stable about this temperature. Although low albite is assumed to be completely ordered at 450°C. a sodium-rich feldspar containing 25 % of potassium feldspar may be much more disordered at this temperature; nevertheless it seems likely that the part of the solvus of SMITH and MACKENZIE is metastable certainly below 500°C.

If it is assumed that the synthetic feldspar solvus is the stable solvus at 660°C. it seems likely that the stable feldspar of composition $Or_{50}Ab_{50}$ is almost completely disordered even at this relatively low temperature. The greater degree of Al/Si order in the sanidine-cryptoperthites may account for the crest of this solvus being lower but it is somewhat surprising then to find that the orthoclase-microperthite solvus is so much higher than either of the other two solvi. In the orthoclase-microperthites the fact that sanidizing is apparently necessary before the crystals can be homogenized implies that in nature the unmixing must have occurred in a feldspar with a more disordered distribution of Al and Si than it now has. In other words for a fairly high degree of Al-Si order to be present the Na and K atoms must have already been ordered at a higher temperature.

On the limbs of the solvus the situation is somewhat different. TUTTLE and BOWEN (1958) found that potassium-rich microperthites were homogenized and unmixed again relatively easily and in a much shorter time than the high-temperature feldspars of the same composition. A possible reason for this is that the limbs of the solvus are in the temperature range in which the stable forms of feldspar are orthoclase and low albite and so unmixing and rehomogenization is accomplished readily.

It appears that when unmixing of Na and K begins at the top of the solvus the feldspars may be completely disordered with respect to Al and Si or some slight order may be present. Both types of ordering will continue together, the Na/K ordering possibly assisting the Al/Si ordering. This view is in direct opposition to that of FERGUSON (1960) who has stated that "... the nature of the framework of the alkali feldspar with appreciable amounts of both Na and K should be determined by the relative amounts of these two atoms present in the structure at the time of Al-Si ordering. Presently some point in the cooling process must be reached where the Al-Si atoms can no longer migrate, and presumably later at some still lower temperature and for some reason not yet understood, perthitization takes place with the segregation of the K atoms into one part of the framework and of the Na atoms into another part". Part of the reasoning used by FERGUSON (1960) in support of this argument is based on the results of heating experiments on pure sodium- and potassium-feldspars and also unmixed feldspars, carried out by a number of workers. From these experiments it appears that the Na and K atoms are moved relatively easily at comparatively low temperatures (500-600°C.) but the Si and Al atoms are only moved by prolonged heating at much higher temperatures (> 1000°C.). It must be remembered, however, that the process of sanidizing a microcline is not an equilibrium process when carried out at about 1050°C. and it may bear little relation to the same process occurring under equilibrium conditions (see accompanying paper by SMITH and MACKENZIE, 1960). Perhaps the strongest argument against the suggestion of FERGUSON (1960) is the fact that no natural low-temperature feldspar (i.e. orthoclase or microcline) with approximately equal amounts of sodium and potassium has been found in a homogeneous, or even a nearly homogeneous, state.

The differences which exist between the three solvi shown by TUTTLE and BOWEN (1958) may be used as a very approximate measure of the degree of Al/Si order in the different forms of feldspar. The indications are that the degree of Al/Si order in the sanidine-cryptoperthites is comparable with that of the synthetic feldspars although it has already been suggested that the natural feldspars show some Al/Si order whereas the synthetic materials are probably almost completely disordered. The orthoclase-microperthites on the other hand give a metastable solvus which is very different from the other two solvi and this is probably due to a very high degree of Al/Si order in the sodium phase and a certain amount of order in the potassium phase.

One further consideration leads us to believe that the synthetic feldspar solvus is more stable than that determined using the natural high-temperature feldspar. A synthetic feldspar held at 600°C., i.e. 60°C below the crest of the solvus, will unmix to two phases: over a period of time some ordering of Al and Si in each phase will take place and it seems extremely unlikely that the feldspar will become homogeneous again as a result of this Al and Si ordering although this would be the consequence if the solvus for the natural high-temperature feldspars was the more stable of the two solvi. It may be noted here that SAHAMA (1960) has recently drawn attention to the considerable difference in temperature (200°C.) between the crest of the experimentally determined solvus in the system $NaAlSiO_4-KAlSiO_4$ (TUTTLE and SMITH, 1958) and that obtained from a study of the unmixing and rehomogenization of natural crystals of the appropriate composition.

YODER, STEWART and J. R. SMITH (1957) have determined experimentally the position of the alkali feldspar solvus at 5,000 bars pressure of water in

experiments of one month's duration and they have concluded that the solvus is raised by about 14°C. per 1,000 bars pressure. If pressure has a significant effect on the position of the solvus this may account for part of the discrepancy between the synthetic feldspar solvus and that obtained by TUTTLE and BOWEN using the natural feldspars since their heating experiments on the natural feldspars were all conducted at a pressure of one bar whereas the synthetic feldspar solvus was obtained from experiments conducted at 1000 bars.

a minimum of temperature for compositions containing about equal amounts of sodium and potassium feldspar. This is based on the belief that substitution of Na and K promotes disorder of the Al and Si atoms, a question which has been mentioned in the preceding section and discussed in some detail in the accompanying paper. This method of denoting degree of order has been adopted because of the existence in the feldspars of phase changes of order higher than the first: it is important to distinguish these from classical phase changes for which a two phase region
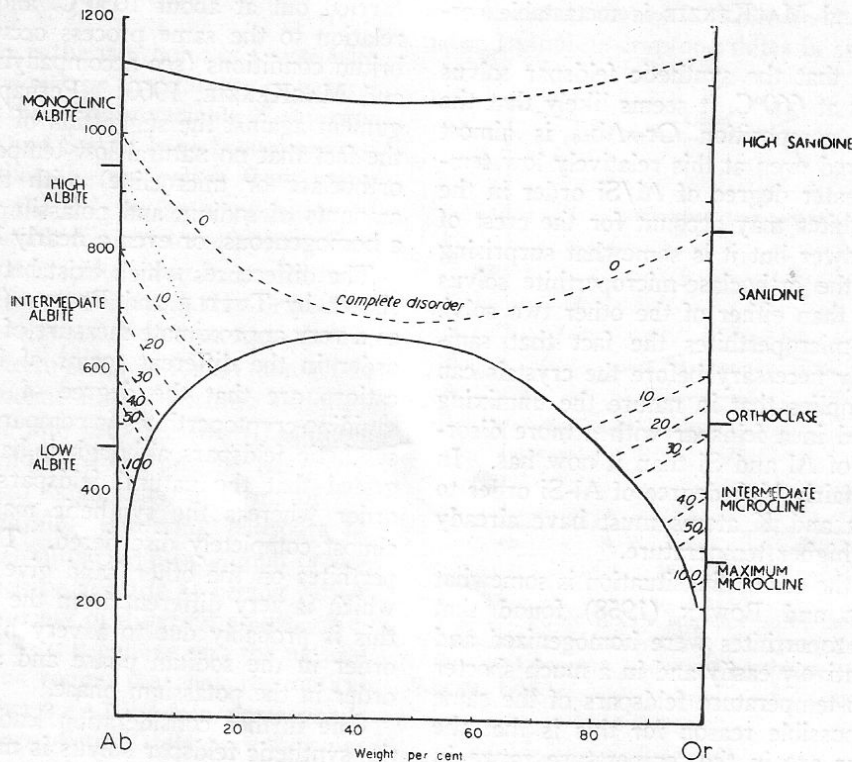
Fig. 3.—The alkali feldspar phase diagram. The dashed curves numbered in tens from 0 to 50 and 100 indicate percentage of Al/Si ordering and the dotted line extending from 950°C. for albite composition to meet the solvus indicates the relation between composition and temperature for the monoclinic-triclinic inversion in sodium-rich feldspars.

THE ALKALI FELDSPAR PHASE DIAGRAM

A number of authors have constructed phase diagrams for the alkali feldspars and have shown either stable or metastable equilibrium relations depending on the cooling conditions. Only one diagram is given here (figure 3) and it is considered to represent the stable phase relations in the sub-solidus region.

A series of curved dashed lines in the diagram are numbered in tens from 0 to 50 and 100 and these represent percentages of long-range Al/Si order, 100 indicating full ordering and 0 complete disorder. The lines representing a high degree of disorder are shown curving down from the end members reaching

depicting the compositions of the coexisting phase can be drawn and no such phase changes exist in the alkali feldspars.

The temperatures for the percentages of Al/Si long-range order for pure sodium feldspar are derived from the data of MACKENZIE (1957): as a first approximation the assumption is made that the X-ray parameter measured by MACKENZIE is linearly related to long-range order. In the case of potassium feldspar the only measure of order which can be used throughout the whole temperature range is the value of the optic axial angle. If it is assumed that the value of optic axial angle is linearly related to degree of long-range order, orthoclase appears to be about 2/3 ordered. From the detailed discussion in the accom-

panying paper it is concluded that a much more likely value for the amount of long-range order in orthoclase is about 1/4. These two values could be reconciled if the value of the optic axial angle depends on short-range order which would be expected to be better than the long-range order.

The criterion which has been used to determine the degree of Al/Si long-range order in the potassium feldspars is given by the expresion

$$\sum_{i=4}^{i=1} \frac{|\, 0.25 - S_i \,|}{1.5} \times 100.$$

This gives the percentage of Al/Si order for a sample if the ratios of $\dfrac{Al}{Al + Si}$ in the four sites S_1, S_2, S_3 and S_4 are known: thus the microcline studied by BAILEY and TAYLOR (1955) is 50 % ordered. The percentages of order for different temperatures have been obtained from figure 5 b of the accompanying paper (SMITH and MACKENZIE).

The crest of the solvus is placed at 650°C. and the equilibrium feldspar of composition $Or_{50}Ab_{50}$ at this temperature is indicated as having almost complete disorder. The limbs of the solvus are drawn through the limits of solid solution as determined approximately by the compositions of homogeneous sanidines (Ab_{40}) and anorthoclases (Ab_{75}) and homogeneous orthoclases (Ab_{15}) (MACKENZIE and SMITH, 1956). By comparison with figure 2 it can be seen that the solvus in figure 3 may be considered as made up of the synthetic feldspar solvus above about 550°C. and the orthoclase-cryptoperthite solvus below this temperature. It seems quite likely that most natural sanidines and anorthoclases have been quenched at a temperature above 660°C. and the unmixing detected in such feldspars has occurred metastable at very low temperature; SMITH and MACKENZIE (1958) have given crystallographic evidence of very low temperatures of unmixing in volcanic feldspars.

The dotted line drawn from about 950°C. for pure albite and intersecting the solvus at about 600°C. represents the monoclinic-triclinic inversion in sodium-rich feldspars and this is undoubtedly a high-order inversion also. Above 950°C. the form of albite is described as monoclinic albite and it is only stable at the high temperature. It has not been designated monalbite because it is uncertain whether this material corresponds exactly to the form of $NaAlSi_3O_8$ which LAVES (1960) has described as monalbite.

Since the temperature scale on this diagram can only be approximate no account has been taken of the possible effects of pressure either on the position of the solvus or on the curves of equal long-range Al/Si order.

EVIDENCE OF STABILITIES OF POTASSIUM FELDSPARS FROM NATURAL OCCURRENCES

A number of investigators have used the feldspars as geological thermometers since BARTH (1934) first proposed the use of the compositions of coexisting feldspars for geological thermometry. We are at present concerned with the reverse process, viz. attempting to obtain more information about the phase relations of the alkali feldspars from observations of their geological occurrence particularly at low temperatures. It does not seem out of place, however, to consider first of all the use of feldspars in geothermometry since so much work has been carried out in this field in recent years (BARTH, 1951, 1956, 1959; HEIER, 1957; DIETRICH, 1960; YODER, STEWART and SMITH, 1957, etc.).

There are two distinct but related methods of using feldspars as indicators of geological temperatures. Firstly, if a relationship between temperature of crystallization and structural state of a feldspar can be established by experimental work then a geological temperature may be obtained from a determination of the structural state of a given feldspar. Secondly, where two feldspars coexist, the compositions of the coexisting feldspars provide a tie line which may be related to experimentally determined tie lines in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$ for a series of temperatures and so a geological temperature can be deduced. A further check on the temperature should be obtainable in the case of two coexisting feldspars by application of the first method to one or both of the feldspar phases. Unfortunately the necessary information is not yet available from experimental work for any but the most approximate indication of geological temperatures by either of these methods. In addition it is fairly clear that high temperature forms of both sodium feldspar and potassium feldspar can form metastably at very low temperatures; the occurrence of three feldspar phases in a rock instead of the expected two phases presents other limitations on the use of the feldspars in geothermometry.

Even if all the experimental data were available the exact significance of the temperatures which may be determined would be uncertain in many cases. DIETRICH (1960) has presented a very useful discussion of the ambiguities attached to temperatures determined from the two feldspar geothermometers and his comments are equally applicable to most other geological thermometers particularly in the lower range of geological temperatures. The same author has concluded that the two feldspar geothermometer is valuable for determining relative temperatures within comparatively small zones in which other variables are less likely to influence the results. Since the chemistry of coexisting feldspars depends not only on their temperature of formation but also on the modification

which is found, DIETRICH has stressed the need for further investigation along this line and it is this aspect to which attention is directed here in the case of the occurrence of two alkali feldspars.

Considering first of all the coexistence of two alkali feldspars, the solvus in the phase diagram is rather flat at the crest and the limbs approach the pure end members rapidly so that 150°C. below the crest of the solvus the compositions of the two coexisting phases are Or_7Ab_{93} and $Or_{79}Ab_{21}$. The evidence for this very restricted temperature interval over which the alkali feldspar solvus may be used for geothermometry lies in the observation that unmixed alkali feldspars generally consist of a fairly pure potassium-rich phase and a nearly pure sodium-feldspar phase or else they are unmixed on a cryptoperthitic scale and we have already given reasons for believing that this is metastable unmixing during rapid cooling. The most significant observation which can be made from the coexistence of two alkali feldspars is the common occurrence of intermediate forms of potassium feldspar, viz. orthoclase and intermediate microclines along with the low temperature form of sodium feldspar, indicating that the temperatures necessary for the same degree of ordering are very much lower for potassium feldspar than for sodium feldspar. These associations can thus be represented on the phase diagram.

In the case of ternary feldspar compositions in which an alkali feldspar and a plagioclase coexist there is a much greater range in temperature over which the compositions of the two phases may be used for geothermometry. For our present purpose, however, very little additional information regarding the stability of the various types of feldspar can be obtained.

Because of the uncertainties in interpreting the geological history of a suite of rocks it is difficult to ascertain what other factors, in addition to temperature, are important in determining the type of feldspar found. The types of potassium feldspar found in pegmatites and granites vary from sanidine-cryptoperthite, through orthoclase-microperthites to microcline-low albite associations either in perthitic intergrowth or as separate crystals. Part of this variation may be due to different initial crystallization temperatures but other factors such as rate of cooling, pressure and volatile content may be of sufficient importance to mask the effect of temperature alone and the minerals found may provide little evidence, either from their compositions or structural state, of the original crystallization temperatures involved. In many cases two or more of the variables mentioned are likely to be interdependent.

EMELEUS and SMITH (1959) in a study of the feldspars in the ring dykes of the Slieve Gullion area investigated the possibility of establishing a relationship between the thickness of a ring dyke and the progress of the feldspars to a low temperature structural state: such a relationship would be expected if cooling rate was the dominant factor in determining the final structural state of the feldspars. EMELEUS and SMITH came to the conclusion that cooling rate was only one factor and local content of volatiles might well be the most important factor in governing the final structural state of the feldspars in these rocks: the great variability of structural state of different crystals from the same hand specimen they considered might be due to the presence or absence of localized concentrations of volatiles.

Since the discovery of the variable obliquity of microclines (LAVES, 1952; MACKENZIE, 1952 a) a number of studies, both optical and X-ray, have been made of the obliquity of microclines and there appears to be a general correlation between obliquity and estimated temperature of formation of the mineral. HEIER (1957) has correlated the boundary between the amphibolite facies and the granulite facies of regional metamorphism with the transition from microcline to orthoclase and he considers 500°C. to be an appropriate temperature for this facies boundary. He has also shown that the obliquity of the potassium feldspars, in the regionally metamorphosed rocks in the Oslo area, has been considerably reduced in the thermal aureole caused by the Permian igneous rocks. CAILLÈRE and KRAUT (1960) have noted, in the granitic rocks near Avallon in France, that orthoclase is the predominant feldspar in the interior of intrusive bodies whereas microcline is concentrated in the peripheral zones and accompanying apophyses. Other studies of this type are progress at the present time.

MARMO (1959) has drawn attention to the common occurrence in orthoclase granites of aplitic dykes and veinlets which always contain a microcline of high obliquity: these dykes and veinlets are much younger than the granite. MARMO concludes that "once orthoclase has been formed, it seems to be as stable as (the) microcline at low temperatures". The present writers prefer to consider that orthoclase may persist "metastably" under conditions in which a microcline of high obliquity may grow and this can almost certainly be explained by the difference in chemical composition of the two phases. The orthoclase in granites will almost certainly have at least 10 % of sodium feldspar in solid solution whereas the microcline is likely to be nearly pure potassium feldspar. From the shape of the dashed curves in fig. 3 it can be seen that the amount of Al/Si disorder increases rapidly with only a slight increase in sodium content and therefore a feldspar of composition $Or_{90}Ab_{10}$ will have a much more highly disordered framework than one which is pure potassium feldspar at temperatures in the region of about 300°C. It seems to the present writers that it is unwise to discuss the relative stabilities of the forms of potassium-rich feldspar in a rock without considering the difference in chemical composition which may exist between the two feldspars.

The orthoclase in this particular case has been described by us as metastable because the chemical composition of the rock has been changed by introduction of material and equilibrium has not been established otherwise two potassium-rich feldspars could not coexist. However, it should be made clear here that it is possible for an orthoclase-microperthite to be the stable feldspar in a rock under the same conditions of pressure and temperature at which a microcline is the stable form of potassium feldspar in another rock, the controlling factor being the bulk chemical composition of the rock.

From the phase diagram (fig. 3) it can be seen that at 450°C. for a bulk feldspar composition more sodium-rich than $Or_{83}Ab_{17}$ the stable feldspar would be an orthoclase-low albite microperthite whereas for pure potassium feldspar composition, the stable form would be an intermediate microcline. The exact shape of the solvus and the nature of the curves of degree of Al/Si order are unknown but would be critical for a more exact discussion of this kind.

The main purpose of the phase diagram presented here is to illustrate the relationship between Al/Si order-disorder and Na/K order-disorder with an approximate temperature scale. The nomenclature used for the forms of sodium- and potassium-feldspar is that which is generally adopted and it is felt that there is at present no necessity for a more elaborate system of nomenclature.

It is hoped that it does not appear from what has been written here that we are being unduly pessimistic about the usefulness of the alkali feldspars in particular and the feldspars in general in elucidating the genesis of rocks in which they occur. We have deliberately stressed the weaknesses and ambiguities in our knowledge of the phase relations in the feldspars to point out the dangers of the too ready acceptance of oversimplified conclusions based on observations either obtained from the study of natural rocks in the field and laboratory, or from experimental investigations of synthetic systems.

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DISCUSSION

LAVES (Zürich):

Several remarks in the preceding paper which could not be discussed orally by the present writer at the Symposium, either because they had not been presented orally or for lack of discussion time, call for clarification and discussion now.

A. Remarks on the *stable* phase diagram of the alkali feldspars presented by MACKENZIE and SMITH (this Symposium, fig. 3).

Many different phase diagrams have been proposed during the time of advances in feldspar research. This very fact is due to the difficulties of experimentally approaching equilibrium states of the feldspars in the laboratory. As the present writer has recently (1960) proposed a phase diagram, here reproduced as fig. 1 of this discussion, some remarks may be appropriate. The main differences between the two diagrams result from the following points:

1. MACKENZIE and SMITH consider apparently (deduced

by the writer from the slope of the dotted line in their fig. 3) only the *displacive transformation* (called by them «the» monoclinic-triclinic inversion in sodium rich feldspars not stating what kind of inversion they mean by this) as impor- tant for a phase diagram without having realized that this transformation may not have any stable equilibrium existence on its own at any temperature or composition (1) (with a theoretical possibility but not necessity that a part of the diffusive transformation line drawn in the phase diagram of the present writer near the sodium side might also be interpreted as a displacive transformation line) and that its temperature/composition dependence in «metastable» phase diagrams has to depend on the Al/Si distribution of the alkali feldspar state considered. (For a detailed discussion of the complex relations here involved see the writers 1960

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(1) It is true, the present writer also included such a line in a phase diagram (1952, p. 561), but becoming aware of the incorrectness of such procedure he corrected his old diagram correspondingly (1960).

paper). Therefore, the dotted line is questionably included in the MacKenzie-Smith- diagram, if it represents only the displacive transformation. If it depicts a stable transformation line, i.e. *the* part of it where a coincidence of displacive and diffusive transformation might be assumed, a corresponding line for the *diffusive transformation* should have been drawn on the potassium side. It is the writer's opinion that the diffusive monoclinic-triclinic transformation (having a
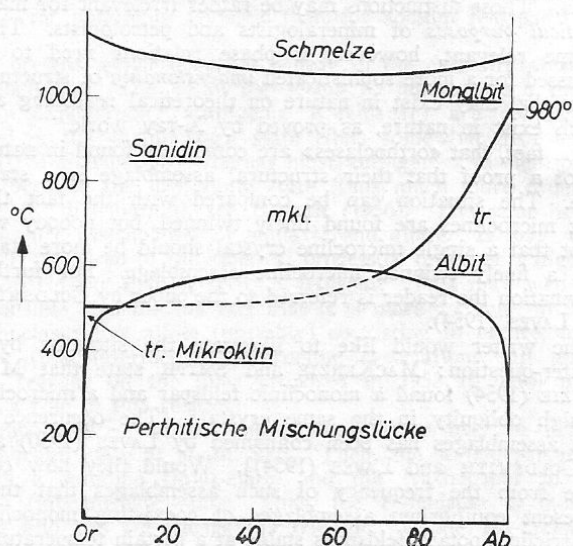

Fig. 1.—Stable phase diagram of the alkali feldspars.

stable temperature for all K/Na-compositions) may be considered as more important for a feldspar phase diagram discussion than the displacive monoclinic-triclinic transformation (which may not have any stability temperature for any composition). At the most it could only coincide in part with the diffusive transformation, starting at pure $NaAlSi_3O_8$ and going to a certain (fixed but experimentally not known) K/Na ratio (2).

It may be objected that the temperature of the diffusive transformation on the potash side (microcline-sanidine) is not known with certainty, and that GOLDSMITH and LAVES (1954) could only suggest, and not prove, that this temperature is approximately 500° C. On the other hand, the diagram of MacKenzie and Smith contains instead of such a transformation line a set of degree-of-Al/Si-order curves the shape and position of which may be even more open to discussion. — In addition, the assumption made by MacKenzie and Smith that $NaAlSi_3O_8$ is virtually fully ordered at 450°C. has not been proven either [it is true, the present writer would agree that this assumption is almost correct but would guess that the temperature of virtually full order would be somewhat lower as a different extrapolation of MacKenzie's (1957, p. 508, fig. 7 and fig. 4 c of the paper by Smith and MacKenzie, this symposium) data appears equally justified].

2. As to the shape of the degree-of-Al/Si order curves just mentioned objections must be raised immediately. These curves have been drawn by MacKenzie and Smith on the assumption that the degree of Al/Si-order depends strongly (in addition to the dependence on temperature) on the K/Na-ratio in such a way that a saucer-shaped dependence results with a minimum at appr. K/Na = 1. The present writer cannot adopt this sort of dependence, inasmuch as no experimental evidence was given. He still believes in the assumptions made in 1952 (p. 560 and 561), that the degree of Al/Si disorder is mainly a function of temperature [because the influence of *one univalent* (K, Na) -ion should be practically negligible compared to the ordering tendencies of the *four high-valent* Al- and Si-ions]. It has been discussed in the paper 1960, however, that a size factor may play a role and a substitution of the K^+ -ion by the considerable smaller Na^+ -ion may lead to a sligh increase of disorder for alkali feldspars in equilibrium at a fixed temperature. Thus, if iso-degree-of-Al/Si-order curves would be drawn in the diagram proposed by the writer [for example using the assumptions based on reasons discussed in the 1960 paper (in connection with the figures 5 and 7, p. 213 and 280)] they would be expected to lie rather horizontally somewhat ascending with increasing Na/K ratio. — It should be realized that in the diagram proposed by the writer (fig. 1 of this discussion) the line depicting the diffusive transformation monoclinic-triclinic as a function of the Na/K ratio is *far from representing* an iso-degree-of-Al/Si-order curve.

3. To add a further complexity: MacKenzie and Smith state

«Above 950° the form of albite is described as monoclinic albite and it is only stable at the high temperature. It has not been designated monalbite because it is uncertain whether this material corresponds exactly to the form of $NaAlSi_3O_8$ which Laves (1960) has described as monalbite».

Indeed, my definition for monalbite differs somewhat from the above one of monoclinic albite, having realized that it might be a chance event if there would be a temperature (assumed to be 950° C. by MacKenzie and Smith), at which the curve for the displacive transformation would coincide with that of the diffusive transformation for pure $NaAlSi_3O_8$. Thus, there are chances that MacKenzie and Smith's definition of «monoclinic albite» is impossible if the diffusive and displacive transformations never coincide in the alkali feldspar phase diagram under equilibrium conditions.

B. On page 55 MacKenzie and Smith (this symposium) state in a foot-note that

«Laves (1960) has redefined his usage of the term analbite so that it no longer corresponds to the form described by Tuttle and Bowen (1950) as highalbite».

This footnote refers to a sentence in which a correlation was given between the «albites» of MacKenzie and those of the present writer.

To avoid further confusions I should comment on this statement in the following way:

1. Tuttle and Bowen (1950) report on *one* form of «high albite». In those days the Al/Si-order concept was not developed as detailed as it is today. Now we know on the basis of several considerations (Laves, 1960), that the synthesis and the natural growth of $NaAlSi_3O_8$ may lead to different forms that can be characterized on strict reasons of structure theory. Two extremes can be defined: (1) Material that *can* become monoclinic by heating rapidly enough to prevent changes of the Al/Si-distribution, called (by the writer) *monalbite* when monoclinic above the temperature of the displacive transformation, and *analbite* when triclinic below the temperature of the displacive transformation and (2) material which *cannot* become monoclinic by heating rapidly enough to prevent changes of the Al/Si-distribution. The latter material is called *albite* if it has an Al/Si-

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(2) The writer likes to acknowledge very valuable discussions he had with Dr. W. L. BROWN on the pertinent problems of this paragraph.

distribution which is possible as a stable one under equilibrium conditions at one definite temperature; it can be subdivided into albite (high), (intermediate) or (low). Innumerable intermediate states not stable under any equilibrium conditions, are possible between these extremes of analbite and albite, viz. states which correspond in principle to those of «adularia» which are intermediate between sanidine and microcline but with Al/Si-distributions that are not stable under any equilibrium conditions. Which states TUTTLE and BOWEN actually had when they X-rayed them at room temperature is not known. The chances are high that they had analbite, albite (high) as well as intermediate states between these extremes, depending on temperature, time and (water-) pressure of synthesis.

2. It may be deplored that the phase relations on the albite side are as complex as they are, but the writer believes that it is better to realize the complexity of facts than to ignore them for the sake of a convenient simplicity.

3. MACKENZIE and SMITH state in the sentence to which the above footnote was given that the term «analbite», redefined by the writer (1960), may correspond to those forms of NaAlSi$_3$O$_8$ which were considered by MACKENZIE (1957) to be metastable. Unfortunately, any reader will look in vain for any definition of what MACKENZIE (1957) considered to be «metastable». Thus the correlation proposed by MACKENZIE and SMITH (this symposium) is without meaning and may add to confusion.

4. The point must be stressed that the ($2\theta_{131}$ $-2\theta_{1\bar{3}1}$) value used by MACKENZIE (1957) to characterize the forms of NaAlSi$_3$O$_8$ cannot be used as a unique criterion, for reasons of principle discussed by the writer (1960: in this paper, only lattice angles were discussed, on which the θ values depend). Perhaps, MACKENZIE was aware of such reasoning, when he wrote his paper. However, he did not make any remark in this respect. He only states once (p. 505) that:

> «two samples of synthetic albite having identical values of $2\theta_{131}$ $-2\theta_{1\bar{3}1}$ may differ in certain physical properties because of differences in their crystallization history.»

The context in which this sentence was written suggests that MACKENZIE thought rather of differences in response to later heat treatments than to differences in structural state.

5. Therefore, because MACKENZIE defines high, intermediate and low albite by the $2\theta_{131}-2\theta_{1\bar{3}1}$ values his correlation with the states of albite (high, intermediate and low), as defined by the writer, is not right. [Compare the statement of BROWN (1960, p. 317): «It is clear that values for $2\theta_{131}$ $-2\theta_{1\bar{3}1}$ can correspond to two completely different states at a fixed composition». See also his figure 14].

C. MACKENZIE and SMITH (this Symposium, P. 58) say (3).

> «It is not clear why LAVES (1960) still states that the mineral which most petrologists would describe as orthoclase is metastable (or unstable) particularly since he frequently describes it as «normal» or

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(3) At final proof-reading it was noticed that the test of p. 58 (left side) was somewhat changed by the authors as the consequence of correspondence. Thus, the sentence quoted, cannot be found any more in the printed version of the paper. Howewer, MACKENZIE and SMITH gave a reply to this C-discussion on page 68, and it would be impossible at this stage to remove the C-discussion as it has been referred to it on other places in this volume.

«common» orthoclase, presumably since it is commonly found as one phase in orthoclase-microperthites».

As to this question I can only express my hope that other readers interested in the subject may be able to understand the reasons why GOLDSMITH, HAFNER and the writer made a distinction between the concepts of «sanidine» and «orthoclase». These distinctions may be rather irrelevant for many *practical purposes* of mineralogists and petrologists. They become relevant, however, if phase relations need to be discussed for a more sophisticated *understanding* of structural states that may exist in nature on theoretical reasoning and which exist in nature, as proved by X-ray work.

The fact, that «orthoclases» are commonly found in nature is not a proof that their structural assemblage is a stable state. The situation can be compared with the fact that most microclines are found finely twinned, but nobody will doubt that a single microcline crystal should be more stable than a finely twinned microcline assemblage. For further information the reader is referred to the paper by GOLDSMITH and LAVES (1954).

The writer would like to illustrate the situation by a counter-question: MACKENZIE and SMITH state that MACKENZIE (1954) found a monoclinic feldspar and a microcline of high obliquity in the same crystal. [The occurence of such assemblages has been confirmed by LAVES (1950) and by GOLDSMITH and LAVES (1954)]. Would they now conclude from the frequency of such assemblages that these represent equilibrium assemblages of coexisting monoclinic and triclinic potash feldspars stable at a certain temperature?

Or another counter-question: MACKENZIE and SMITH's (1956) observation that sodium-rich alkali feldspars can be found in nature the optics of which are intermediate between orthoclase-microperthite and sanidine-cryptoperthite, due to the existence of two forms of exsolved NaAlSi$_3$O$_8$ is another example of a very finely divided assemblage of domains in twinned orientations where some overall coherency of the NaAlSi$_3$O$_8$-framework may be expected with the result that such assemblages may have quite a persistency over geologic times. I hope, even MACKENZIE and SMITH will not propose that such assemblages should be considered as stable ones. At least they did not yet reserve a field for them in their proposed stable phase diagram discussed above (under A.).

D. MACKENZIE and SMITH (this symposium) reproduce as fig. 2 a «Solvidiagram» of TUTTLE and BOWEN (1958). With respect to this figure it has to be pointed out, that the solvus lines for the orthoclase-cryptoperthites should not be considered as a «solvus» because the Al/Si-distribution in the «orthoclase» is different from the one in the exsolved NaAlSi$_3$O$_8$-phase. For a given difference in the aforementioned distributions the position of the lines has to depend on the bulk composition with respect to the K/Na ratio. Thus, the relative position of such lines has to depend in principle on two factors: (1) on the difference in the Al/Si-distribution of the two phases and (2) on the bulk composition with respect to the K/Na ratio. A detailed discussion of this situation was already given in 1952 (p. 564, 4). In addition, factors such as size, shape and orientation of the exsolved components may play a role.

Thus, such lines cannot even be considered as representing metastable solvus relations of a binary system; the situation is analogous to the temperature dependence of the distribution of two dyes in a mixture of oil and water where oil and water correspond to the two different AlSi$_3$O$_8$-frameworks, and the two dyes correspond to the Na and K ions. Thus, the slopes of the lines in fig. 2 have to depend on the framework 1/framework 2 ratio and on the Na/K ratio. Such lines may represent the mixing and unmixing behaviour of *one particular specimen* but they cannot be considered as being characteristic for a binary system as plotted in fig. 2.

E. On page 62 MacKenzie and Smith (this Symposium) state:

> «The most significant observation which can be made from the coexistence of two alkali feldspars is the common occurrence of intermediate forms of potassium feldspar, viz. orthoclase and intermediate microclines along with the low temperature form of sodium feldspar, indicating that the temperatures necessary for the same degree of ordering are very much lower for potassium feldspar than for sodium feldspar.»

The present writer does not believe in the necessity of such a conclusion. The following seems to him a much more likely explanation: authigenic K-feldspars are frequently found in the «orthoclase» state (thus somewhat disordered re Al/Si-distribution) whereas most authigenic Na- feldspars are found in the low albite state (thus much more ordered re Al/Si distribution), see Baskin (1956). The same holds for fissure assemblages of adularia and albite. It may well be that the *speed* of the kinetical process of ordering is higher in Na-feldspar than it is in K-feldspar. This may well be responsible also for the fact that it is more common to find «orthoclase»-low albite (unstably) coexisting in nature, than albite (high-intermediate)-microcline associations. In addition, reasons on the lines proposed in 1952 (p. 446) may play a role in this respect:

Suppose a K-feldspar and a Na-feldspar may be in an equilibrium state at about 500°. Then, the K-feldspar may be in a sanidine (low)-state, and the Na-feldspar in an albite (intermediate)-state. Thus, the K-feldspar is monoclinic and the Na-feldspar is triclinic. If the Na-feldspar has not grown initially as a monalbite, one may assume that it be a triclinic single crystal. As cooling proceeds the K-feldspar has to increase in order by changing from monoclinic to triclinic symmetry, whereas the Na-feldspar increases in order without changing symmetry. Thus, the K-feldspar has to make up its mind whether to change into a «left» or into a «right» orientation (whereas the Na-feldspar does not need to). The K-feldspar evades this decision by developing the «orthoclase»-state, a finely twinned mixture of «right» and «left» domains with some overall lattice coherency [«orthoclase» in the sense of Laves (1950, 1952); Goldsmith and Laves (1954); Laves (1960); Laves and Goldsmith, this symposium]. Such a state may be able to exist unstably for a considerable length of time because (1) it would have to surpass the energy barrier of creating incoherent domain boundaries for the formation of triclinic units of rather large size and because (2) such a domain-«recrystallization» would require quite an additional diffusion process, as 50 % of the already triclinicly ordered «left» domains have to change into «right» ones or vice versa. On the other side, the Na-feldspar already exists at 500° C. as a triclinic single crystal and can proceed continuously with increasing its order without having the difficulties any truly monoclinic K-feldspar is faced with when cooled below, or metastably grown below, the transformation temperature of the diffusive transformation (monoclinic → triclinic).

Thus, different *speeds* of aproaching the stable state may well be responsible for the above quoted observations and the present writer does not see any necessity of accepting the indications deduced by MacKenzie and Smith which may have been one of the reasons why they have drawn their iso-degree-of-Al/Si-order curves in their phase diagram the way they did.

F. For similar reasons as argued in the preceding paragraph the present writer objects to the influence of Na on the persistency of «orthoclase» as a major factor. MacKenzie and Smith say (p. 62).

> «The present writers prefer to consider that orthoclase may persist «metastably» under conditions in which a microcline of high obliquity may grow and

this can almost certainly be explained by the difference in chemical composition of the two phases. The orthoclase in granites will almost certainly have at least 10 % of sodium feldspar in solid solution whereas the microcline is likely to be nearly pure potassium feldspar.»

Contrary to MacKenzie and Smith's viewpoint the writer believes the explanation will almost certainly be the following: «Orthoclase» is persistent because of its finely twinned structural state. As its overall Al/Si-disorder is higher than the one of microcline it admits Na in solid solution more than microcline does. When the delicate metastable persistency of its structural state becomes disturbed enough during its geological history (be it by time, changing temperature or by the influence of accessories like water, etc.) it «recrystallizes» into enlarged (mostly visibly twinned) microcline domains. As a consequence of this Al/Si ordering process «the phase» microcline is formed and a microcline-albite (low) solvus becomes effective, i.e. the Na will be thrown out by this process (cf. the papers by Goldsmith and Laves and by Laves and Goldsmith, this volume).

G. At the end of the paper MacKenzie and Smith state:

> «From the phase diagram (fig. 3) it can be seen that at 450° for a bulk feldspar composition more sodium-rich than $Or_{83}Ab_{17}$ the stable feldspar would be an orthoclase-low albite micropertite whereas for pure potassium feldspar composition, the stable form would be an intermediate microcline.»

In the light of the fact, that the shapes of the curves drawn in the quoted «stable» phase diagram are constructed on the base of questionable assumptions (see A, 2; E and F above) this rather definite statement should be met with proper reserve.

MacKenzie (Manchester) and J. V. Smith (Chicago). Answer:

A. Of course, it is recognized that the phase diagram proposed by us is merely an interpretation of imcomplete experimental data, and we welcome discussion of its features.

The problem of the stability relations of albite (and adjacent K-Na feldspars) will only be solved by more experiments. Laves and his co-workers have not yet published any data on attempts to reverse the changes that occur by heating albite near the melting point. Furthemore the occurrence of a shell of glass on crystals of monalbite (Brown, 1960) suggests accidental heating above the melting point. Only when the reactions have been followed in both directions and without formation of glass will it be possible to draw firm conclusions. Furthermore, it would be desirable to X-ray the crystals at high temperatures rather than quenching to low temperatures, a difficult but not impossible task.

Regarding the monoclinic-triclinic inversion in albite, for any particular K/Na ratio the feldspar will undergo the transition either by the diffusive or the displacive process, but not both unless they happen to coincide. Until further experimentation gives data on the diffusive transition in Na-rich feldspars (no reliable data exists at the moment) it seems safest just to use the data for the displacive transition. At least these data do fit the observations for natural feldspars from volcanic rocks (Laves, 1952; MacKenzie, 1952 b; MacKenzie and Smith, 1956). If the diffusive transition is shown by experiment to occur at a higher temperature than the displacive transition then, of course, the displacive transition has no place on a stable phase diagram. It is hoped that Laves and his co-workers will undertake further

experiments both on pure albite and on K-containing albites to elucidate these reactions.

The main contribution of the diagram proposed by us is the addition of contour lines of Al-Si order to show the assumed non-first order transition from the disordered to the ordered state. There is no need for us to repeat the arguments why we consider that the contours bend in sympathy with Na-K substitutional disorder. But we would wish to point out that if Na and K ions had no effect on Al-Si ordering the ordering relations of Na- and K-feldspars would be the same. Field and experimental data suggests to us that disordering in K-feldspar commences at a lower temperature than in Na-feldspar (though LAVES is not convinced by our arguments), possibly by as much as 200° C. Furthermore we wish to point out that both ordered and disordered feldspars contain one univalent ion and four high-valent Al and Si ions. It is the tiny differences in the chemical forces that determine the temperature and compositional dependence of ordering, not the absolute magnitude of the forces. Unfortunately there seems no hope of calculating the resultant energy differences between ordered and disordered forms because our knowledge of chemical forces is so primitive. It is hoped that our suggested variations of Al-Si order with composition will encourage experimentation to test this idea. Naturally we hope that the variation assumed by us will be correct, but if not, we still think that the idea was worth proposing in that it encouraged the carrying-out of the experiments.

B. We hate to add to the confusion by making further comments! We are troubled by the nomenclature used by LAVES as examination of Fig. 1 (of this discussion, not the original text) will show. In fig. 1 we have plotted ordering against temperature. There will be some curve (ABC) relating the equilibrium ordering with temperature. The exact shape of this curve is not known but if MACKENZIE's data of 1957 are right it would have a shape similar to that given here. Anyway the exact shape is not significant. Crossing this curve will be the curve DBE for the monoclinic-triclinic inversion, which may be either displacive or diffusive over its length. The exact position of this curve is not known but it should slope the way it does in Fig. 1,
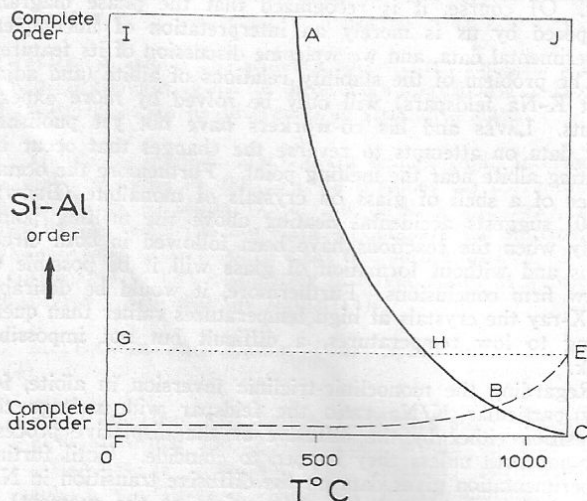

Fig. 1.—See text for detailed explanation. Ordering is assumed to be complete at 450° C. in accordance with the extrapolation of the data obtained by MACKENZIE in 1957. The melting point of albite has been assumed to be independent of order and near 1100° C., thus the line JEC represents the metastable melting point and C the true melting point. It has also been assumed that the feldspar is completely disordered just below the melting point.

otherwise certain triclinic feldspars would become monoclinic on cooling, whereas all evidence points to the opposite conclusion. According to the statements made by LAVES in this discussion, feldspars in the area DBECF are called monalbite while those in area DBEG are called analbite (this is the consequence of B 1 (1)). The consequence of B 1 (2) is that the term albite covers only feldspars that lie on the portion of the curve AH. Thus the equilibrium form of albite according to this definition would change from albite (low) to albite (high), then to analbite and finally to monalbite. This consequence violates the conclusion by LAVES that analbite does not occur on the stable phase diagram (LAVES, 1960, Fig. 7). The discussion here is oversimplified in that we have assumed only one ordering parameter. Actually there can be an infinite number of ways of ordering as LAVES has suggested. Consequently the situation is even worse than is shown here. Fortunately all natural specimens of K- and Ca-bearing sodium feldspars from volcanic rocks so far examined give values for the monoclinic-triclinic displacive inversion that fit well on curves that assume a simple unique variation with composition (MACKENZIE and SMITH, 1956). Until this relation is proved to be more complex we shall continue to use the definition of anorthoclase given in that paper. If it is proven to be more complex we shall, of course, agree that modifications are needed.

In summary we do not feel able to accept LAVES' nomenclature for sodium feldspars because we believe that his scheme is inconsistent and because we believe that the experimental data is inconclusive. We hope that further experiments will be undertaken.

In an attempt to relate the various synthetyc forms of albite, obtained in MACKENZIE's (1957) experimental studies, to the new nomenclature proposed by LAVES (1960), MACKENZIE and SMITH stated that the term analbite may be equated with those forms of $NaAlSi_3O_8$ which were considered by MACKENZIE (1957) to be metastable.

LAVES notes that the reader will look in vain for any definition of what MACKENZIE (1957) considered to be metastable. It was clear from the experimental results published that for each temperature there was a gradual approach to a fixed value of $2\theta(131) - 2\theta(1\bar{3}1)$ and the crystals having this fixed value were described as «supposed equilibrium forms». It was not established that equilibrium was established in any of the experiments on the crystallization of a glass of $NaAlSi_3O_8$ composition and it certainly was not established that any of the phases produced were stable phases. However the change in the value of $2\theta(131) - 2\theta(1\bar{3}1)$ with time and the eventual attainment of a fixed value of $2\theta_{(131)} - 2\theta_{(1\bar{3}1)}$ does suggest that all the intermediate forms are metastable although it indicates nothing about whether the final «supposed equilibrium form» is the most stable form of $NaAlSi_3O_8$ for the particular physical conditions of each experiment.

LAVES has also questioned the use of the value of $2\theta_{(131)} - 2\theta_{(1\bar{3}1)}$ to characterize the forms of $NaAlSi_3O_8$ as proposed by MACKENZIE (1957) since a number of different structural states may have identical values of $2\theta_{(131)} - 2\theta_{(1\bar{3}1)}$. This is so obvious from figs. 3 and 4 of MACKENZIE's paper (1957) that it was not considered essential to elaborate on this point. The simplest method of detecting these structural differences available at the present time is to study the effect of heat treatment and so this aspect was stressed. The statement of BROWN (1960, p. 317), quoted by LAVES, «It is clear that values for $2\theta_{(131)} - 2\theta_{(1\bar{3}1)}$ can correspond to two completely different states at fixed composition» adds nothing to what has already been stated by MACKENZIE (1957). If it is assumed that the extrapolated products of MACKENZIE's (1957) syntheses at constant temperatures represent the stable forms of $NaAlSi_3O_8$ for each temperature and that $2\theta_{(131)} - 2\theta_{(1\bar{3}1)}$ is uniquely related to order for these forms then low, intermediate and high albites can be

described by this function if they are stable forms. It should perhaps be emphasised again that this is strictly speaking applicable only to pure $NaAlSi_3O_8$.

C. The main reply to this section of discussion has been given elsewhere in our replies. Studies of feldspars from many granites and metamorphic rocks show that orthoclase, as a constituent of orthoclase-perthites, is a very common mineral, and because of this we think that it has a structure that is either the stable one or very near to the stable one at some intermediate temperature. If not, one would expect to find that orthoclase was a less common mineral. According to our investigations of feldspars from many localities the assemblage orthoclase plus microcline of high obliquity is not common, and may therefore be a consequence of unusual conditions.

On the question about the occurrence of two sodium-rich phases in certain perthites, and the omission of a place for them on our phase diagram: the phase diagram is for Ca-free alkali feldspars whereas the natural perthites contain several per cent of $CaAl_2Si_2O_8$. We believe that the presence of Ca considerably modifies the relation between potassium and sodium feldspars. Thus there is no inconsistency in our proposals.

D. In discussing the solvi diagram of TUTTLE and BOWEN (1958), LAVES states that the solvus line for the orthoclase-cryptoperthites «cannot even be considered as representing metastable solvus relations».

It seems clear from a statement by LAVES (1960) that he uses the words «stable» and «equilibrium» as if they were synonymous when he states: — «The distributions are sub-divided into 'stable' and 'unstable' ones, a distribution being called stable if there is a temperature at which it can exist under equilibrium conditions». This statement neglects the fact that an equilibrium curve may correspond to metastable equilibrium. TUTTLE and BOWEN (1958) were able to reverse

the solution and exsolution of the two feldspar phases in orthoclase-cryptoperthites by heating and cooling experiments; they therefore established that the solvus was an equilibrium curve. That it represented metastable equilibrium for most of its range of temperature they deduced because they had already obtained a solvus for what they considered to be the more stable phases, viz. the synthetic feldspars, in the temperature region of 600° C.: this conclusion is supported by MACKENZIE & SMITH in this symposium.

Factors considered by LAVES such as the difference in the Al/Si distribution of the two phases, the size, shape and orientation of the exsolved components have nothing to do with equilibrium but may affect the rate of attainment of equilibrium.

E. Although we appreciate LAVES' argument, we prefer to rely on our interpretation of the geological evidence. No useful purpose would be served by going into this in detail here, as we have a long publication planned on the significance of the petrologic data for the alkali feldspar phase diagram.

F. See discussion to SMITH and MACKENZIE, point 4.

G. It should be noted that we used the conditional «would» not the definite «is», thus recognizing the uncertainty in our conclusions. However, we welcome LAVES' remark so that we can clarify our statement.

LAVES (Zürich), Reply to B:

MACKENZIE and SMITH believe that my scheme of $NaAlSi_3O_8$-nomenclature is «inconsistent». I do not. Readers may decide.

Polymorphism, order, disorder, diffusion and confusion in the feldspars

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ABSTRACT

In the course of the last years several papers [Ferguson, Traill, Taylor: Acta Cryst. 11 (1958) 331; Megaws Min. Mag. 32 (1959) 226; Ferguson: Canadian Mineralogist (1960)] have sought to show that ideas expressed by the present authors concerning the orthoclase-microline relations and the polymorphism of anorthite are wrong. To avoid further confusion differences and identities of opinion are discussed in the light of new experimental work and theoretical considerations. Some of the confusion may be due to different interpretations of the meaning of term «orthoclase».

At the moment, there is a good deal of discussion on problems of the feldspars and a certain amount of confusion is apparent. With the risk of adding to the confusion by further contributing to the discussion, we should like in part to stress anew some old ideas and in part present some unpublished data, all on the alkali feldspars.

In fig. 1 the Al/Si-positions in the $AlSi_3O_8$-framework as determined by Taylor (1933) are shown. In the monoclinic case there are A and B positions only, whereas with triclinic symmetry A_1, A_2, B_1, B_2 positions must be distinguished. [These are equivalent to the Si_2, Si'_2, Si'_1, Si_1 of Taylor's original work; Megaw (1956) has used a more sophisticated terminology changed somewhat in a later paper (Megaw, 1959). The A-B-terminology is used here for the sake of simplicity].

It is known that the structural differences in the alkali feldspars are related to the Al/Si-distribution in the two or four A and B sites. All evidence points to a continuous gradation of properties between the low- and high-temperature states, indicating a continuous variation in the distribution of Al and Si between the A and B sites. No evidence against this interpretation has come to our attention.

This is shown diagrammatically for the K-feldspars in Figure 2. These curves which are fully discussed by Laves (1960), give the probabilities a, b (a_1, a_2, b_1, b_2) of finding Al atoms in the positions A, B (A_1, A_2, B_1, B_2) as a function of temperature. In addition to this set of curves which may be taken as representative for stable states, i.e. distributions under equilibrium conditions, an infinite number of sets is possible from a structural point of view, characterizing states that are not stable under any conditions.

Limiting our attention at the moment to the K-feldspars, it is quite obvious that there are truly monoclinic structures, generally called sanidines. There are also definitely triclinic structures, the microclines.

Let us now consider the possible relationships of these two structural types to the controversial orthoclase.

The main points of our arguments and the experimental evidence supporting them are presented in several papers [Laves (1952), Goldsmith and Laves (1954 a and b), Hafner and Laves (1957), Laves
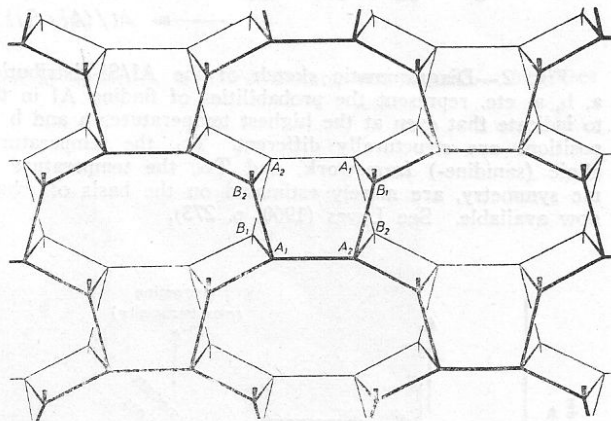
Fig. 1.—Projection of the Al, Si positions of the $AlSi_3O_8$-framework in the direction of c*, i.e. on the plane (001). See Laves (1960, p. 268).

(1960)] and are summarized here; they are based on the study of a great variety of natural and synthetic feldspars subjected to extensive heat treatments and investigated by several methods.

a) $KAlSi_3O_8$ can exist in a highly disordered state as sanidine (high) and in a highly ordered state as microcline (low, or maximum microcline).

b) Intermediate states with intermediate degrees of order link sanidine (high) with microcline (low).

Laboratory experiments have proved the existence of a *continuous* sequence of intermediate states between the triclinic and monoclinic structures.

c) The investigation of natural K-feldspars has confirmed the existence of intermediate states in nature. Many degrees of "triclinicity" ranging bet-
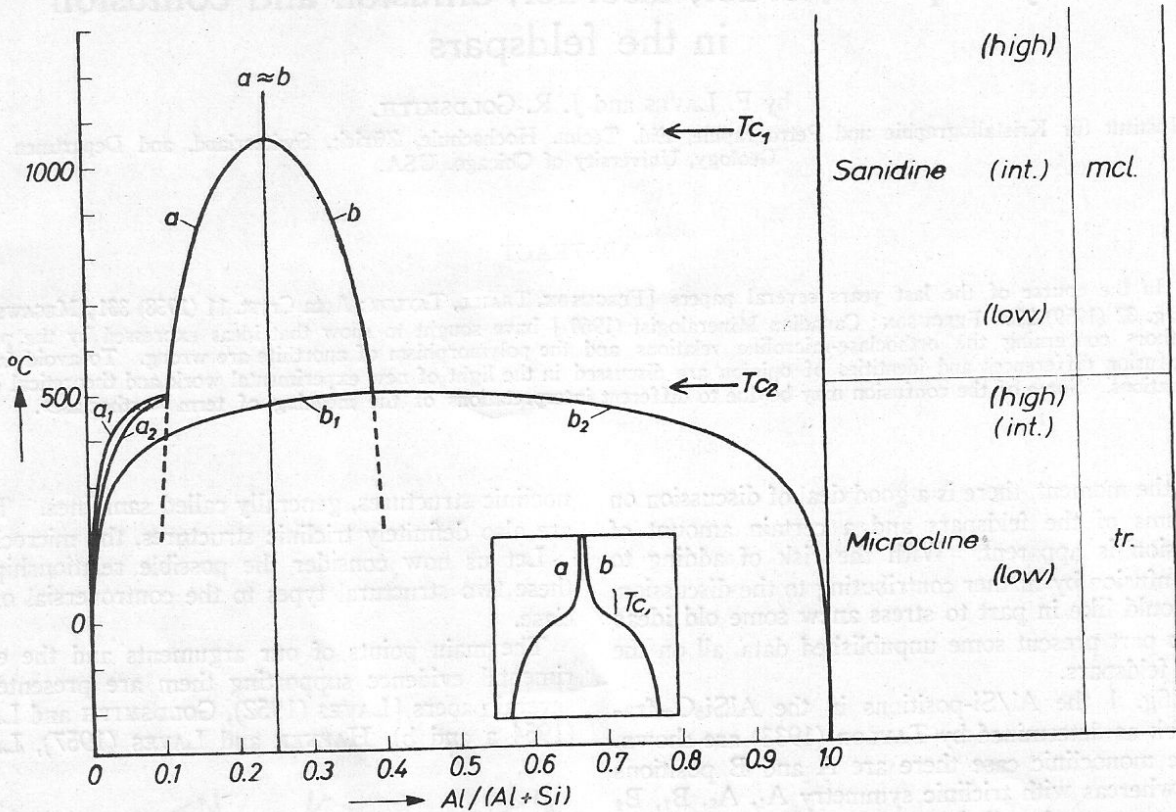
Fig. 2.—Diagrammatic sketch of the Al/Si-distribution for $KAlSi_3O_8$ under equilibrium conditions. The curves a, b, a_1 etc. represent the probabilities of finding Al in the point positions A, B, A_1 etc. The small insert is drawn to indicate that even at the highest temperatures a and b may very well not be exactly equal, because the A and B positions are structurally different. Tc_1, the temperature where a noticeable ordering should set in within the monoclinic (sanidine-) framework, and Tc_2, the temperature at which the ordering process necessitates the reduced triclinic symmetry, are merely estimated on the basis of what appears reasonable plus the limited experimental evidence now available. See Laves (1960, p. 273).
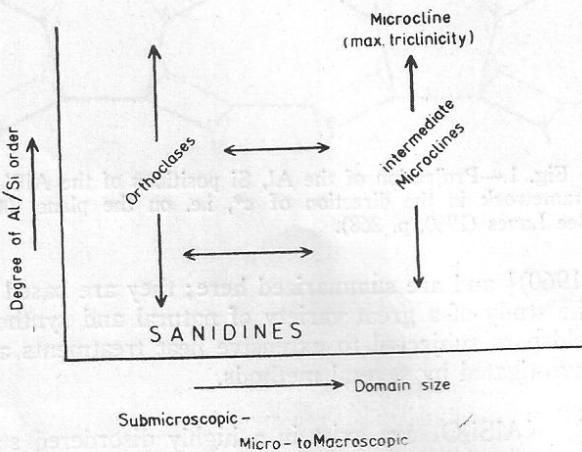
Fig. 3.—Diagrammatic representation of K-feldspar relations. On the left side «Degree of Al/Si order» refers to short range order, on the right side to both short range and long range order. See Goldsmith and Laves (1954 b, p. 116).

ween 0 and 1 were found, indicating a continuous change from the monoclinic state to that of maximum microcline taking place in nature in the course of adjustment to equilibrium conditions.

d) Most microclines are twinned in such a way that it can definitely be stated that they originally grew as monoclinic crystals.

e) Obviously, *there must be states* between truly monoclinic sanidine and those microclines in which the triclinic character becomes observable. It is self-evident that the ability to observe the triclinic character depends on the resolution of the instruments available, on the degree of the triclinicity of the twinned domains and on the size of the domains. We define "orthoclase" as material that deviates from a truly monoclinic sanidine but that "appears" to be monoclinic because of triclinic domains too small to be resolved by the microscope or even by X-ray diffraction, in which

the domains are related to each other by the albite twin law or by the pericline twin law or by both laws in the typical microcline fashion. The per-

tinent relations are expressed in Fig. 3. The term "common orthoclase" has been used to avoid confusion, inasmuch as some use the term "ortho-

C 2/m
Sanidines

P2₁/a–Domain–State

(unit cell–"TWINNING")

C1̄

TWINNED Microcline

● = more Al than in O
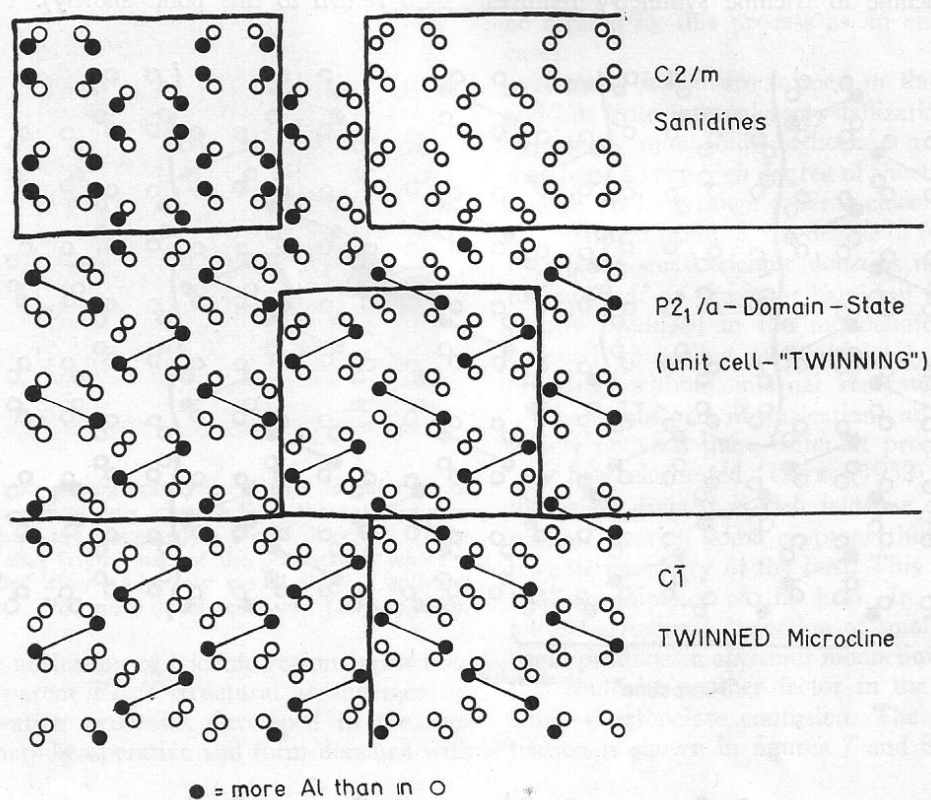
Fig. 4.—Diagrammatic representation of the Al/Si-distribution in sanidines, in a P2₁/a-state, and in microclines (see fig. 1 for the positions chosen).
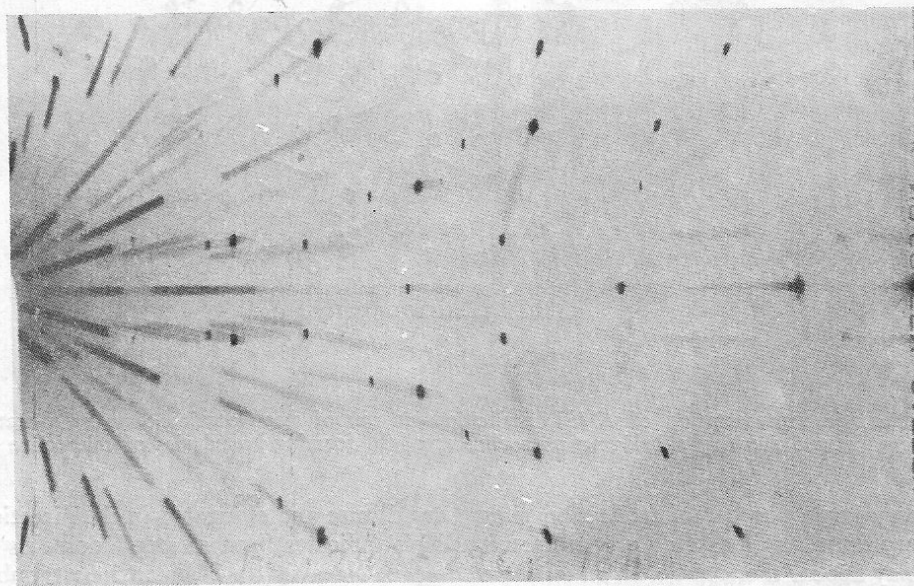
Fig. 5.—Oscillation diagram of an adularia with diffuse (h + k = odd) reflections. Fe radiation; oscillation axis = b.

clase" for all K-feldspar that is or appears to be monoclinic, including sanidine.

The ordering process involved in the transformation from monoclinic to triclinic symmetry requires

space group $P2_1/a$ (see fig. 4). There is indeed some experimental evidence for this state, as "orthoclases" have been reported (LAVES, 1950) showing X-ray reflections (see fig. 5) hkl with $h + k = $ odd. (We shall return to this point shortly). These reflections

(a)

"Microcline"

(b)
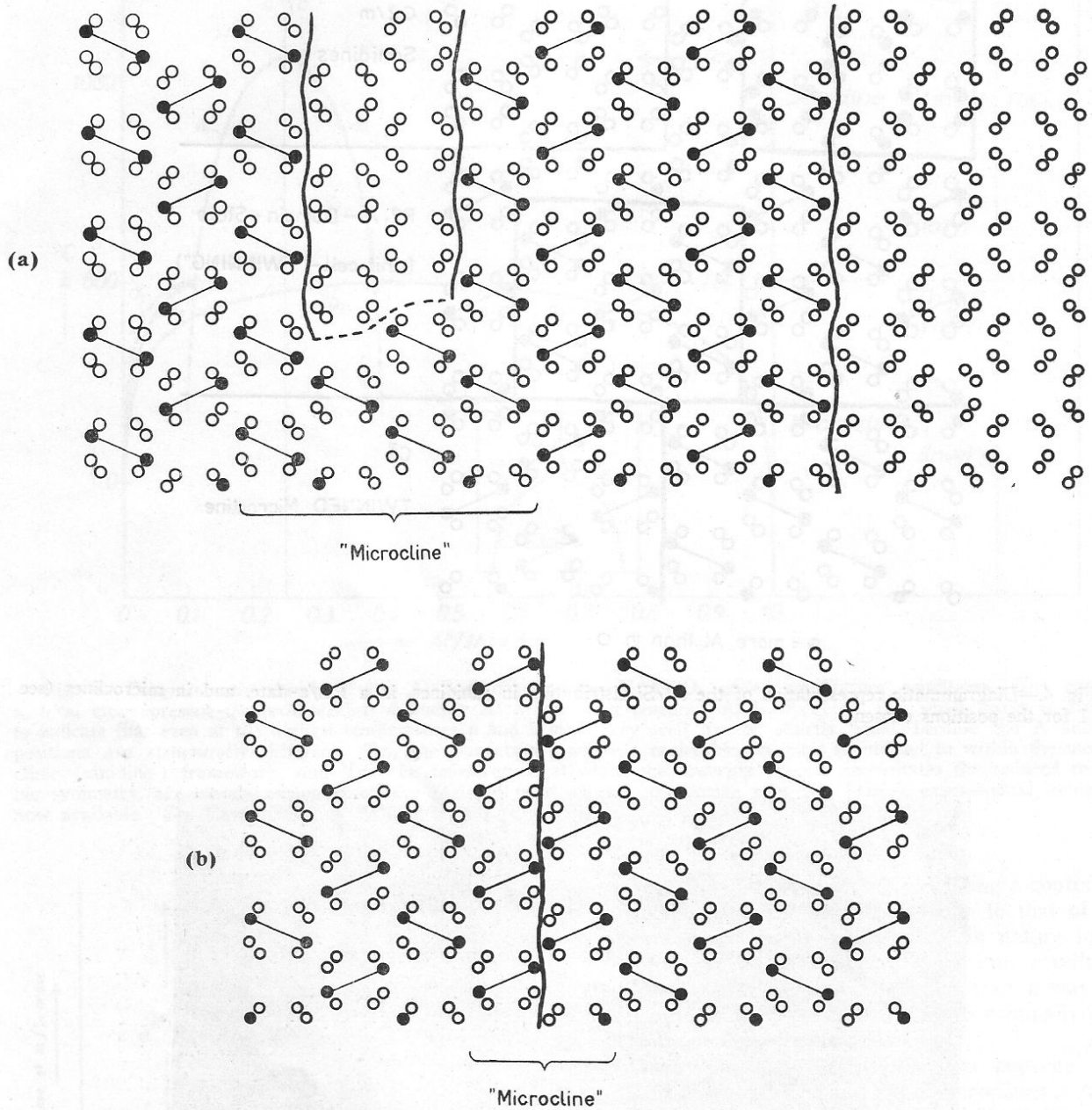
"Microcline"

Fig. 6.—Diagrammatic representation of Al/Si-distributions in out of step domains of a $P2_1/a$-state, (a) separated within a sanidine matrix and showing a bridging microcline area, (b) forming boundaries of microcline character.

nucleation. If a very large number of nucleation sites are produced, a very fine domain assemblage will result and the material may appear monoclinic. In an extreme case the domains may be essentially of unit cell size, in which case the material would have the monoclinic

are diffuse and elongated in the direction of the b-axis. This indicates "out of step" domains as illustrated in fig. 6. Note that a 2-dimensional double-layer of "microcline" parallel to (010) exists at the domain boundary. These boundaries may act as sites from which

continued development ("internal recrystallization") of coarser microcline domains *can* take place. This does
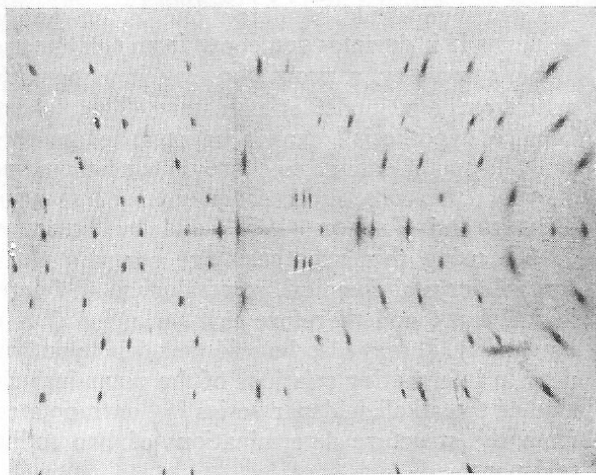
Fig. 7.—Oscillation photograph (central part is cut out) of an adularia with diffuse tails starting from the «monoclinic» maxima. The tails are elongated in the b*-direction. They appear only on that (right) side of the photograph where a microcline twinned after albite law would show a splitting of the reflections. For more detail see LAVES (1950, p. 566).

not imply that nucleation of triclinic regions *must* take place from a parent P2₁/a-structural arrangement.

Other nucleation processes developed in the monoclinic host may be operative and form domains with triclinic (microcline) symmetry. These can also grow by some process of internal recrystallization to virtually any size and eventually produce microcline with macroscopic twinned units. Single crystals may even be formed by this process as an end-product in rare cases.

If many nuclei are formed in the monoclinic host, and but little internal recrystallization takes place, an apparently monoclinic orthoclase may develop which may have a very high degree of short range order, even though the long range order is close to zero. However, as illustrated in fig. 3, the degree of (short range) order within the small triclinic domains may also vary continuously. If on the other hand but few nuclei are originally produced in the monoclinic host, a coarsely twinned microcline may ultimately be developed by ordering, without internal recrystallization.

The mechanism of nucleation and growth may vary widely between these different processes.

It has been noted [LAVES (1952), p. 565/567] that the finely divided K-rich feldspar exsolved from the triclinic host of some cryptoperthites also shows the triclinic geometry of the host. This is due to the controlling influence of the host. In analogous fashion mutual structural distortion of small triclinic domains could produce an apparent monoclinic geometry. Thus, this could be another factor in the monoclinic —triclinic— orthoclase confusion. The reality of this situation is shown in figures 7 and 8.
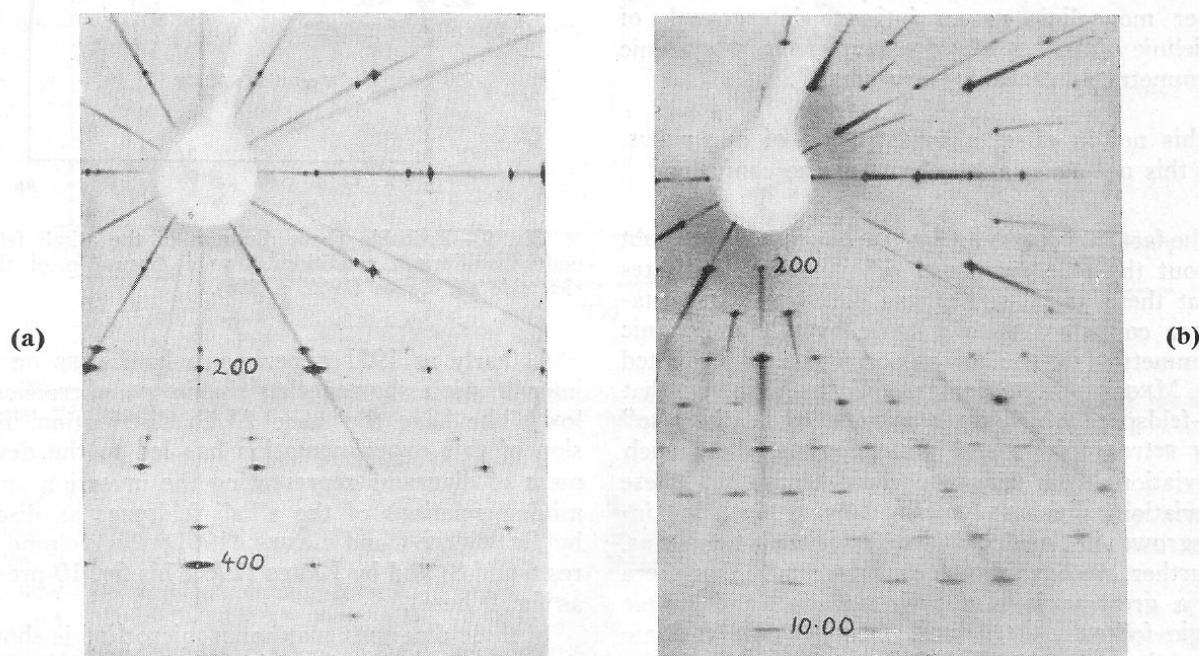
Fig. 8.—Precession photographs of an optically monoclinic adularia with *c* as precession axis (a) Cu-radiation: Note that 200 is rather sharp having only a very weak tail, whereas 400 shows in addition to a sharp spot (note the β-reflection) a rather strong tail. (b) Mo radiaton: Visible are 200, 400, 600, 10.00 (800 is extinct). Note that 10.00 consists only of a symmetrical tail without central spot. Measurement of the ends of the tail would lead to a γ* characteristic of maximum microcline.

We have been criticized by FERGUSON, TRAILL and TAYLOR (1958), by MEGAW (1959) and by FERGUSON (1960), and it may be that some of the differences of opinion are due to confusion over the meaning of the *word* "orthoclase". Little need be said relative to the paper by FERGUSON, TRAILL and TAYLOR (1958), inasmuch as they merely state that they do not believe our interpretations with the questionable implication that we have produced no experimental data. The microcline problem will be discussed shortly, but we would like to state the following with respect to orthoclase:

1) If K-feldspar *is* monoclinic, having the space group C2/m, we call it sanidine.
2) If an orthoclase exists which differs from the model we have proposed, and differs from microcline, it must be proved that it is a distinct structural type, i.e. a polymorph that would differ from a sanidine in some distinctive structural feature. A difference in degree of order within the confines of the space group C2/m is not regarded by us as sufficient unless it can be shown that there is a first order discontinuity leading to a distinctive phase.
3) In the abstract on "The structure of orthoclase" by JONES and TAYLOR (1960; this symposium, distributed at Copenhagen; see the corresponding paper —1961, this volume— presented by MEGAW) it was stated that "No final decision is reached on the true symmetry of orthoclase-whether monoclinic or an intimate intergrowth of triclinic units, but any departure from monoclinic symmetry is probably very small".

Is this not in effect a confirmation of our views, and is this not again at the heart of the confusion?

4) The fact that JONES & TAYLOR express some doubt about the true symmetry of orthoclase, indicates that there are X-ray effects that violate expectations consistent with a truly overall monoclinic symmetry (see the corresponding paper presented by MEGAW, this volume). We have shown that K-feldspars which are usually called "orthoclase" by petrographers and mineralogists, show such deviations from true monoclinic symmetry. These deviations are best explained by an intimate intergrowth of submicroscopic triclinic domains. Further, we have shown experimentally that there is a great variety of such material, and simple logic following structural theory would indicate that there can be an infinite variety of such deviations, linking the truly monoclinic sanidine to the visibly crosshatched microcline. Thus *one* structure determination of *one* "orthoclase" —as interesting as it may be— does not add anything to the principle of the models we have proposed.

If the structural determination shows the specimen to be truly monoclinic, without diffuse tails originating from the normal monoclinic reflections, the specimen would be merely one of the sanidine series. If it deviates somehow from truly monoclinic symmetry, a proof showing it to be different from our model is necessary. The "charge balance hypothesis" cannot be regarded as theoretically sound enough to shore up the lack of such a proof; the consequences derived by FERGUSON, TRAILL and TAYLOR (1958) and by FERGUSON (1960) using this hypothesis are contrary to observable crystal-chemical, mineralogical and petrological facts, and therefore cast serious doubts on its validity. It may also be said that this hypothesis used in interpreting relations of the potassium-rich side of the alkali feldspar series is "extrapolated" from the structure determinations of two sodium feldspars.
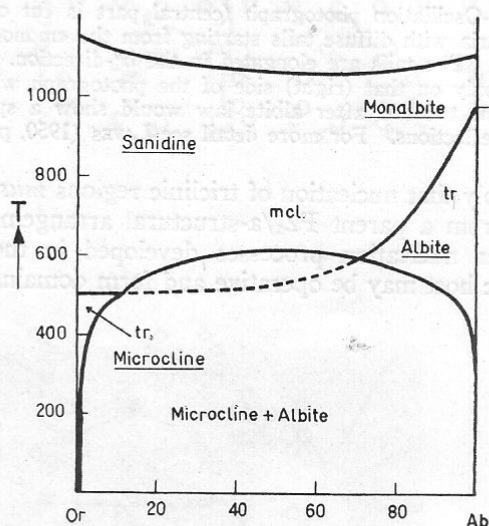
Fig. 9.—Probable phase diagram of the alkali feldspars under equilibrium conditions. For a discussion of the Na rich side see Laves (1960, p. 288).

As early as 1951 experiments by LAVES on alkali interdiffusion showed that maximum microcline and low-albite have the same Al/Si distribution. Extension of this experimentation has led to the development of diagrams representing the inversion and unmixing relations of the alkali feldspars as discussed by GOLDSMITH and LAVES (1961; this volume, figures 6 and 8) and by LAVES (1960, his fig. 10 presented as fig. 9 here).

In these diagrams maximum microcline is shown as the stable modification of sodium poor alkali feldspars. All evidence points to this as a fact. In conflict with all known evidence, FERGUSON, TRAILL and TAYLOR (1958) state that a predominance of Na is required for the formation of anything like maximum microcline. They believe any triclinic microcline to be uns-

table at any temperature and therefore should under equilibrium conditions eventually become monoclinic "orthoclase". FERGUSON's (1961) abstract in this Symposium [see the full paper (1960)] indicated that this point of view is still supported.

FERGUSON also states that the stable, essentially pure K-feldspar is a slightly ordered monoclinic orthoclase. Yet it is now clear that the orthoclases of igneous and metamorphic rocks contain significant

In addition Fig. 11 shows a thin-section photograph of an adularia with an albite-content of appr. 5 % throughout the crystal. All gradations from monoclinic material, to virtually maximum microcline are visible and it is evident that the triclinic parts have developed from monoclinic ancestry. Many other lines of evidence could be brought to bear against the charge-balance hypothesis (see MACKENZIE and SMITH, 1959), but only one more fact will be mentioned here:
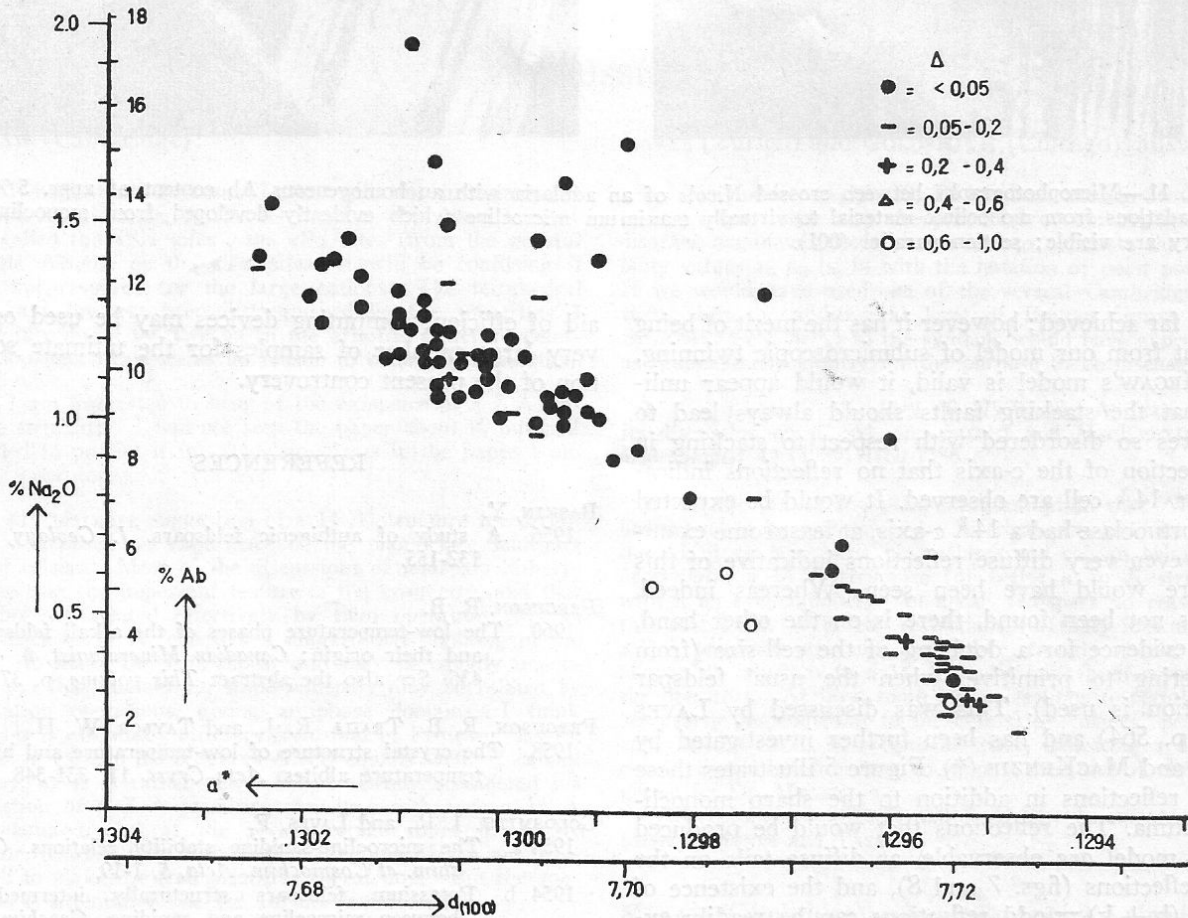
Fig. 10.—d $_{(100)}$ versus Na content, chemically determined, of adularias from the Swiss Alps, selected at random. Note that triclinic character is statistically stronger at low than at high Na contents.

amounts of Na in solid solution, whereas the microcline phases of rocks of these types are essentially sodium free.

Some new evidence further counters the FERGUSON, TRAILL and TAYLOR point of view. Fig. 10 shows Na content (chemically determined) versus a^* for 50 adularias selected at random from Alpine localities. Cores and rims have been separately investigated. Solid circles represent material commonly called orthoclase, crosses represent material with triclinic X-ray behaviour. It is evident that the triclinic material has lower Na content than the "monoclinic" material.

the existence of essentially Na-free highly triclinic authigenic microclines (BASKIN, 1956) is fatal to the FERGUSON, TRAILL and TAYLOR hypothesis.

Quite another argument has been put forth against our orthoclase model by MEGAW (1959) who extends a stacking fault concept to orthoclase that she originally proposed for plagioclases. Her suggestion culminates in proposing a 14Å c-axis for orthoclase, admitting not only that it has not been observed but that it may not even be observable. This model for orthoclase is said to be experimentally indistinguishable from whatever orthoclase is, within the limits of accu-

(a) (b)
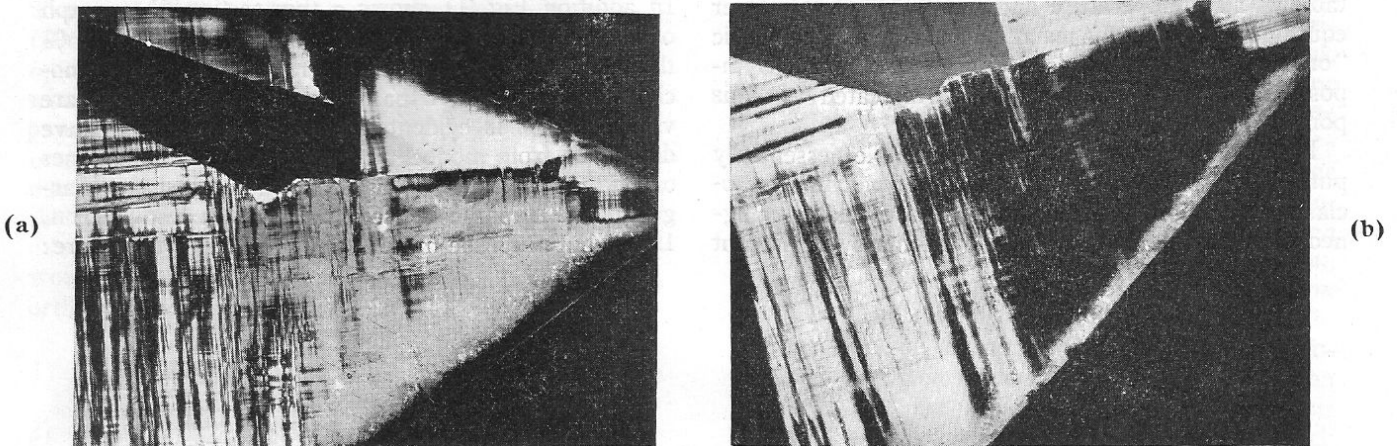
Fig. 11.—Microphotographs between crossed Nicols of an adularia with an homogeneous Ab content of appr. 5%. All gradations from monoclinic material to virtually maximum microcline which evidently developed from monoclinic ancestry are visible; section parallel (001).

racy so far achieved; however it has the merit of being different from our model of submicroscopic twinning.

If Megaw's model is valid, it would appear unlikely that the stacking faults should always lead to structures so disordered with respect to stacking in the direction of the c-axis that no reflections indicative of a 14Å cell are observed. It would be expected that if orthoclase had a 14Å c-axis, at least some examples of even very diffuse reflections indicative of this structure would have been seen. Whereas indeed, this has not been found, there is on the other hand, strong evidence for a doubling of the cell-size (from C-centering to primitive, when the usual feldspar orientation is used). This was discussed by Laves (1950, p. 564) and has been further investigated by Smith and MacKenzie (*). Figure 5 illustrates these diffuse reflections in addition to the sharp monoclinic maxima. The reflections that would be produced by our model *are* observable, as diffuse tails on the main reflections (figs. 7 and 8), and the existence of diffuse (h + k) = odd reflections can be readily explained by the logical extension of our orthoclase model to material with very small domains (see Figs. 5 and 6).

Two approaches to some of the complex problems of the feldspars may be contrasted. On the one hand the crystal structures of relatively few specimens may be determined in considerable detail with continuing refinement. On the other hand what we consider to be infinite variability in feldspars may be examined from a less detailed but more coherent point of view, using any pertinent technique in addition to X-ray diffraction.

The time may come when some observational technique is fast and sure and direct, and with the probable

aid of efficient computing devices may be used on a very large number of samples for the ultimate solution of the present controversy.

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DISCUSSION

MEGAW (Cambridge):

1. I hope that Profesor LAVES will not introduce the notation on his slide, $A_1 B_1 A_2 B_2$, for what have hitherto been called the «Si» sites , the «B» sites (from the general formula AB_4O_8) or the «T» sites; it will be confusing if A is not reserved for the large cations. The tetrahedral sites have hitherto been distinguished by the subscripts 1 and 2 introduced by TAYLOR in the original structure determination, and there seems no reason to change this notation.

2. I am interested to hear of the existence of a 7 Å primitive structure. I had not seen the paper about it, but had been led to predict it for the plagioclases in the paper I am giving later today.

3. My tentative suggestion of a 14 Å structure for orthoclase was based on experience of the plagioclase feldspars and of celsian. Most of the discussions of feldspars hitherto assume that the important feature is the symmetry, and that domains are related effectively by twin operations. From experience of 14 Å feldspars I suggest that doubling of the subcell to make the true repeat unit may be equally important, and that domains in some feldspars may be related by translation operations, giving antiphase domains. I think this idea is essentially different from that of Professor LAVES, but might explain his observed effects equally well. I cannot yet say, as it is rather new. I had already considered his suggestion of a 7 Å primitive structure rather than 14 Å body-centered, and at the present stage think it equally possible, because they both involve doubling of the primitive subcell to make the true primitive repeat unit. But the suggestion is a tentative one for further consideration.

4. With regard to the question of submicroscopic twinning I would go perhaps rather further than Dr. TAYLOR and say that I cannot see that this particular orthoclase is intermediate between sanidine and microcline, because some of the individual atomic parameters and bond lengths are *not* intermediate. Neither can they be explained as intermediate between the two twinned orientations of microcline in any way that I can see; I tried this at an earlier stage of refinement without success, and JONES and TAYLOR searched for it in the final coordinates. Hence from the point of view of this structure determination there is no meaning in describing the material as a twinned microcline.

5. The structure determination ignored the weak streaks; to that extent, it certainly refers to an average structure. But experience with celsian showed that ignoring *sharp* reflections gave a satisfactory average structure, where the coordinates represented the mean of the two actual positions. Hence we believe the positions in this orthoclase determination to represent reliable mean positions of the true structure.

LAVES (Zurich) and GOLDSMITH (Chicago), answer:

1. The notation A_1, A_2, B_1, B_2 has been used to demonstrate in a most simple way the principles of our Al/Si order/disorder arguments, because we had to correlate the probability values a_1, a_2, b_1, b_2 with the notation of point positions. If we would have used one of the several Cambridge notations, then the addition at least of Roman figures (as in $Si^I_1, Si^I_2, Si^{II}_1, Si^{II}_2$) to the symbols would have appeared to us unnecessarily clumsy for the purpose to be discussed.

2. Cp. LAVES, *J. Geology* **58** (1950), fig A, plate 2 and its discussion on p. 564, and SMITH and MacKENZIE, *Am. Mineralogist* **44** (1959) 1169-1186.

3. If one makes the plausible assumption that Al tetrahedra tend to be surrounded by Si tetrahedra and vice versa, the Al/Si ratio in basic plagioclases and celsian being $\approx$ 1 *necessitates* a 14 Å structure (or better a 7n Å structure, with n an even number). In alkali feldspars no reasons of this sort exist. Whereas reflections (diffuse) indicative of a 7 Å *primitive* structure are rather strongly visible (see 2. above), no allusions to a 14 Å repeat have been reported in the literature. At least some h01 reflections (especially planes nearly perpendicular to the c-axis) or "planes" perpendicular to the c-axis in reciprocal space, indicating a doubled c-axis, should be observable to support the point of view suggested by Dr. MEGAW.

With respect to points 4 and 5 see our comments on the paper by JONES and TAYLOR.

MEGAW (Cambridge), comment on point 3 above:

(a) The Al/Si ratio in anorthite does not *necessitate* the loss of the body-centring, yet it *is* lost; this constitutes a doubling of the cell.

(b) When antiphase domains occur, they weaken all difference reflections equally, irrespective of their direction in reciprocal space.

(c) My hypothesis is that there is *some kind* of doubling of the unit cell, whether this is done by making the 7 Å face-centred cell into 7 Å primitive or into 14 Å body-centred, or by some other doubling not yet envisaged. The evidence quoted by LAVES and GOLDSMITH makes the first alternative more probable, but is not finally conclusive.

LAVES (Zurich) and GOLDSMITH (Chicago), reply:

To (b). As far as diffuseness is concerned (which is important as far as observability of reflections is concerned)

Dr. Megaw's statement holds only for domains having an isometric shape (in Dr. Megaw's 1959 assumptions an anisotropic shape was implied).

To (c). Our model of orthoclase is supported by X-ray evidence. Dr. Megaw's model (rather definitely proposed in 1959 to contrast ours) turns now out to become a rather indefinite one. The once suggested doubling of the c-axis has changed to "*some kind* of doubling of the unit cell". *Our* X-ray observations are considered by Dr. Megaw to be "not finally conclusive". On the other hand, Dr. Megaw cannot give *any* X-ray evidence for *any* of her suggestions.

Megaw (Cambridge), note on reading the manuscript of the paper by Laves and Goldsmith, June 1961:

If the diagrams in fig. 4 (middle section) and fig. 6b represent the authors idea of the structure of orthoclase, it is not very different from mine. This is a perfect structure, with two subcells in the unit cell; fig. 4, middle section, shows a single domain, and fig. 6b part of two domains, with an out-of-step boundary wall. I cannot, however, see any reason for calling it a submicroscopic twin of microcline. If the definition of microcline is based on detailed atomic coordinates, these are not necessarily exactly the same in the new structure; if it is based on a particular pattern of Al-rich sites, this is certainly *not* the same, as shown in the figures. With the doubled repeat period, there are other possible patterns of Al-rich sites which perhaps should be considered; the pattern shown may be the most plausible.

Where I disagree with the authors is in their concept of "domains of unit cell size", which I think is a misinterpretation of the meaning of domains. Domains are regions of perfect structure, separated by walls where there is some sort of misfit. The energy in the walls is different from that in the interior. If the interior regions are so small that they do not even contain one unit cell uninfluenced by the walls, they are no longer pieces of perfect structure and cannot properly be called domains. To regard a subcell as the limiting case of a domain, as is done here, is misleading. Where, as here, there is a perfect alternation of two different subcells, the region over which alternation is perfect constitutes the domain. There is no reason why domains of orthoclase should not be mixed with domains of microcline, as in fig. 6a.

Laves (Zurich) and Goldsmith (Chicago), reply:

We fully agree with Dr. Megaw's domain definition However, how small may a domain be? — We believe it to be legitimate (for the sake of a theoretical discussion of structural relations between a domain model in the usual sense and a perfect structure in the usual sense) to use a concept «domain of unit cell size» if the context makes it clear what is meant. This was thought to be the case in formulating the sentence in question which reads unabridged «In an extreme case the domains may be essentially of unit cell size, in which case the material would have the monoclinic space group P2₁/a (see fig. 4)».

The Sodium Content of Microclines and the
Microcline-Albite Series (*)

by JULIAN R. GOLDSMITH and FRITZ LAVES (**)
University of Chicago.

ABSTRACT

An X-ray method for determining the amount of $NaAlSi_3O_8$ in solid solution in microcline (triclinic $KAlSi_3O_8$) is described. The complete microcline-albite solid solution series has been prepared by alkali interdiffusion in the solid state, although this series is metastable over most of its compositional range. The lattice angles of several intermediate compositions were determined by the Buerger precession technique, and show a non-linear change with composition.

The equilibrium relations of the alkali feldspars in the fields of the low-temperature modifications (microcline and albite) are considered and probable unmixing and ordering relations are discussed.

A variety of potassium-rich feldspars have been examined by X-ray methods. The data on hand indicate that most microclines have exsolved virtually all of their albite, and have 5 percent or less $NaAlSi_3O_8$ in solid solution.

INTRODUCTION.

Most of the microcline of plutonic rocks, metamorphic rocks, and pegmatites is macro- or micro-perthitic. For this reason the amount of $NaAlSi_3O_8$ in solid solution in microcline proper has been uncertain. The problem of separation of the microcline from the albite makes any chemical methods of analysis suspect, and any satisfactory optical method would ultimately depend upon correlation of optics with materials of known composition and structure. Microcline has not been synthesized, so that it has not been possible to use this direct method of obtaining material of known composition.

The compositional range of microcline and the relation of composition to temperature has considerable petrologic significance. The equilibrium relations between the low temperature modifications in the system $KAlSi_3O_8$-$NaAlSi_3O_9$ (i.e., the microcline-albite relations) are unknown, and it would be highly desirable to know the configuration of the solvus. This investigation was carried out as a first step in the evaluation of the microcline-albite equilibrium relations. A method for determining the $NaAlSi_3O_8$ content of microcline is described, and data on a number of microclines are presented. In addition, some of the geometrical structural relations of an artificially produced

metastable solid solution series between microcline and albite are discussed.

THE MICROCLINE-ALBITE SERIES

A number of intermediate compositions in the series microcline-albite have been artificially prepared by alkali interdiffusion in the solid state. These compositions were prepared both as finely divided materials suitable for X-ray powder diffraction, and as small crystalline units suitable for analysis by single-crystal techniques. Materials for powder diffraction were prepared by carefully mixing weighed quantities of finely powdered microcline and finely divided glass of the albite composition. In several mixtures, powdered albite was used, mixed with $KAlSi_3O_8$ glass. The mixtures were tamped into small platinum capsules and heated at temperatures and for times sufficient to produce equilibrium alkali exchange between the crystals and the glass. The heating schedules to be described presently were however of insufficient severity to induce any observable development of a high-temperature state in the Al-Si framework of the end-member feldspars. It is assumed that the intermediate compositions behave similarly in this respect. The material for single crystal work was prepared by tamping small microcline crystals or crystal fragments (approximately 0.1 mm in the largest dimension) in a matrix of finely divided glass of the albite composition and heating as above. Alkali exchange between the crystals and glass matrix could be carried to completion, or gradations in crystal composition could be produced as a function of time and temperature of the heat treatment. This technique is similar to that used earlier by LAVES (1951) to show the essential similarity in the Al-Si frameworks of microcline and

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albite. In addition, a number of intermediate compositions were prepared by heating natural microcline perthites, to be described presently.

The lattice constants of microcline and albite (LAVES. 1952, table 2, p. 551) show that the greatest change in spacing would be expected in planes with a large a-axis contribution. Inspection of powder patterns of microcline and albite led to the choice of the (400) reflection as a convenient measure of composition. This reflection is of sufficient intensity to be readily observable and of a high enough order to be rather sensitive to compositional change (1). The shift of this reflec-

by the high-temperature alkali feldspars than to assume a straight line relation. The validity of this assumption has been checked by preparing Na-containing microclines of known composition, and the derivation of a working curve for Na-containing microclines follows.

A METHOD FOR DETERMINING THE NA-CONTENT OF MICROCLINE.

Is has recently been observed that authigenic K-
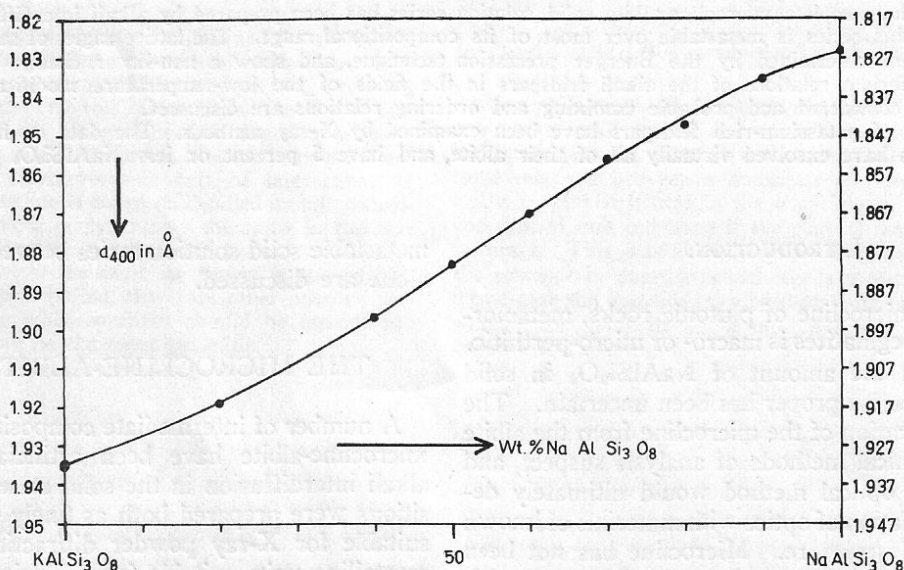
Fig. 1.—Curve of the (400) spacing (left ordinate) vs. composition for the high-temperature (synthetic) alkali feldspar series, data derived from DONNAY & DONNAY, 1952. See discussion in Appendix II, indicating that the absolute values of d(400) shown in this curve may be too high by approximately 0.003 Å (right ordinate).

tion was quite obvious in the artificially prepared intermediate members of the microcline-albite series.

One might assume a near linear relationship between composition and (400) spacing, such as that shown by BOWEN and TUTTLE (1950) for the (201) reflection in the sanidine-analbite (high-temperature albite) series. However, the data of DONNAY and DONNAY (1952) on the high-temperature series show that the a-axis spacings plotted against composition deviate from a straight line. In Fig. 1 the curve is drawn through the points determined by DONNAY and DONNAY for the synthetic high-temperature series (2). It is perhaps more logical to assume that the change in lattice constants of microcline produced by the substitution of Na for K would be more like that shown

(1) For microcline d(400)= 1.927 (LAVES, 1952, p. 551), albite d(400) = 1.820 (COLE, et al., 1951, p. 23). See apendix II for further discussion of these spacings.

(2) The values of d(400) were derived from the tabulated a* values of DONNAY and DONNAY (1952), those for the K- and Na end numbers being 1.9349 and 1.8280.

feldspars from several localities are virtually pure, single-phase microclines (BASKIN, 1956). In several occurrences the microcline shows maximum triclinic geometry, thus the lattice constants of pure (3), fully triclinic microcline have been established (BASKIN, 1956, also see LAVES 1952, p. 551). The authigenic microcline from a Swiss dolomitized limestone (Pontiskalk) has been used as a standard in the present work. The differences in the lattice constants of the triclinic microcline and of pure monoclinic $KAlSi_3O_8$ (sanidine) were established by comparing the Pontiskalk microcline with sanidine prepared in two ways: 1) By hydrothermal crystallization of $KAlSi_3O_8$ glass, and 2) by sanidinization of the authigenic microcline itself, by heating it at 1050° C for at least one month. The value of the a parameter, as indicated by the spacing of the (400) reflection, is slightly greater in sanidine than in microcline of the same composition. This was observed and measured by registe-

(3) $NaAlSi_3O_8$ content is approximately 1-2 percent.

TABLE I

(400) SPACING DIFFERENCE BETWEEN MICROCLINE AND SANIDINE

Initial Material	Treatment to produce sanidine	$\Delta d_{(400)} =$ d (Swiss microcline) - d (Sanidine)
1. $KAlSi_3O_8$ glass ... ... (2 runs)	Crystallized 625°C, 900 atm. H_2O, 19.5 hrs.	— 0.0076; — 0.0032
2. $KAlSi_3O_8$ glass	Crystallized 600°C, 1000 atm. H_2O, 24 hrs.	— 0.0054
3. $KAlSi_3O_8$ glass	Cryst. as 1. above, then heated 1050°C, 4 days.	— 0.0048
4. Swiss authigenic microcline ... ... (3 runs)	Heated 1050°C, 1 month.	— 0.0054; — 0.0032 — 0.0063
5. Swiss authigenic microcline	Heated 1050° - 1060°C, 4 months.	— 0.0032

Average $=$ — 0.0049

ring the X-ray powder diffraction patterns of the monoclinic and triclinic materials on the same film. A Nonius quadruple Guinier-type focussing camera was used, in which four samples can be simultaneously irradiated (4). The Pontiskalk microcline was used as a standard in all of our work; one of the four positions was always filled with this standard, and X-ray spacings of interest were measured in terms of their deviation from the equivalent spacing of the standard microcline. Spacings determined by the powder method are thus given in terms of $d_{(microcline\ standard)} - d_{(unknown)} = \Delta d$, rather than in direct spacing units, to avoid instrumental errors, shrinkage, etc.

Table I presents the data on the (400) spacing

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(4) Co radiation was used, monochromatized with a bent quartz crystal. The effective DEBYE diameter of the camera is 229 mm. All measurements were made at room temperature.
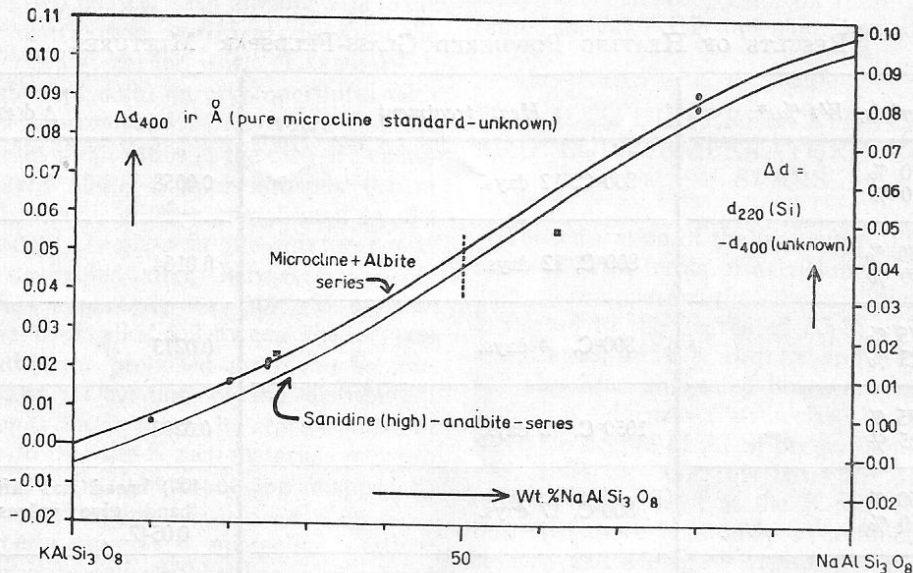
Fig. 2.—The upper curve is the derived curve (see text) for the microcline-albite series. The lower curve is that for the high-temperature series, as in Fig. 1. The ordinate is the relative spacing of the (400) reflection, referred to that of the Swiss authigenic microcline as the standard. See Appendix II for reference to a silicon standard. The space between the two curves represents the (400) spacing differences in the high- and and low-temperature series, which at the $KAlSi_3O_8$ end is the difference between fully triclinic microcline and the monoclinic sanidine (— 0.0049). Microcline with intermediate values of triclinicity would fall on intermediate curves.—The data of Table II are plotted as circles (and a dashed line), and data from Table III as squares.

The values of the right ordinate refer to silicon as a standard (see Appendix II).

differences between microcline and sanidine. The value of 0.0050 is taken as the (400) spacing difference between the most oblique triclinic form and the monoclinic high-temperature state of $KAlSi_3O_8$.

The difference in the (400) spacing of albite and analbite (a high-temperature albite) was also determined. Measurements were made on two samples of virtually pure albite (AMELIA COURTHOUSE, Va., and Pala, California) against the Swiss microcline standard, and $\Delta d_{(400)}$ with respect to microcline was determined to be 0.1059. Using the data of DONNAY and DONNAY (1952) for pure high-temperature $NaAlSi_3O_8$, a value of 0.0040 is obtained as the (400) spacing difference between albite and analbite. This value was also found to agree, within our limits of error, with the spacing difference observed between the albite samples and the (400) spacing of a synthetic analbite crystallized hydrothermally from $NaAlSi_3O_8$ glass at 455° C for 19 hours.

The curve of $d_{(400)}$ vs. composition in the sanidine-analbite series (fig. 1) can now be shifted (raised and slightly tilted from its position in fig. 1) to match the d-spacing of the end members microcline $(1.9349 - 0.0050 = 1.9299)$ and albite $(1.8280 - 0.0040 = 1.8240$; see foot-note 2). The relationship of the proposed microcline-albite curve to the sanidine-albite curve (in terms of Δd) is shown in fig. 2.

The separation of the 2 curves of fig. 2 can be represented in terms of a fictitious approximately 7

percent $NaAlSi_3O_8$ content at the pure $KAlSi_3O_8$ end. This could be referred to as the triclinicity (GOLDSMITH and LAVES, 1954 a) correction: a pure, fully triclinic microcline would appear to have approximately 7 percent $NaAlSi_3O_8$ in solid solution if the spacing value for the high-temperature (monoclinic) modification of DONNAY and DONNAY (1952) were used (5).

RESULTS OF (400) SPACING MEASUREMENTS ON MICROCLINE-ALBITE SOLID SOLUTIONS.

Several compositions in the microcline-albite series were prepared by:

1) heating mixtures of finely powdered authigenic microcline and $NaAlSi_3O_8$ glass; 2) heating a mixture of finely powdered crystalline albite and $KAlSi_3O_8$ glass; 3) heating fragments of 2 natural samples, a microcline perthite and an albite-microcline anti-perthite. The crystalline-glass mixtures 1) and 2) were

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(5) Shortly before this manuscript was put in press, Professor J. V. SMITH kindly called our attention to the fact that he had suggested (SMITH, 1956, p. 53) that there was a systematic error in the spacing measurements by DONNAY and DONNAY on the high-temperature series of alkali feldspars. SMITH states: «The corrected values of 2θ were, on the average, about 0.025° higher than those given by DONNAY and DONNAY». (Cu radiation.)

TABLE II

RESULTS OF HEATING POWDERED GLASS-FELDSPAR MIXTURES

Initial Materials, Wt % *	Heat treatment	$\Delta d_{(400)}$
Swiss microcline 90 % NaAlSi₃O₈ glass 10 %	800°C, 12 days.	0.0058
Swiss microcline 80 % NaAlSi₃O₈ glass 20 %	800°C, 12 days.	0.0164
Swiss microcline 75 % NaAlSi₃O₈ glass 25 %	800°C, 4 days.	0.0213
Swiss microcline 75 % NaAlSi₃O₈ glass 25 %	1050°C, 2 days.	0.0203
Swiss microcline 50 % NaAlSi₃O₈ glass 50 %	800°C, 17 days.	(400) broad and diffuse. Extremes of band give values of 0.0384 and 0.0547.
Amelia Albite 80 % KAlSi₃O₈ glass 20 %	850°C, 4 days.	0.0909
Amelita Albite 80 % KAlSi₃O₈ glass 20 %	1000° — 1020°, 2 days.	0.0871

* The differences between mol and weight percents in the alkali feldspar series are small, and within the limit of error of the X-ray method used for measurement.

TABLE III

DATA ON HOMOGENIZED PERTHITES

Locality	Spectrochemical Analysis (*)	Composition from Alkali ratio	Heat treatment	X-ray powder data
Pellotsalo	Na$_2$O 2.9 % K$_2$O 12.0 % CaO 0.17 %	Ab + An 26 % Or = 74 %	800°C 15 months	(400) somewhat broadened. Δ d = 0.0233 ; corresponding to 27 % NaAlSi$_3$O$_8$ (**)
Wisconsin	Na$_2$O 6.9 % K$_2$O 6.0 % CaO 0.5 %	Ab + An 62 % Or = 38 %	1000°C 4 days	(400) quite broad and diffuse. At center of band : Δ d = 0.0555 ; corresponding to 54 % NaAlSi$_3$O$_8$ (**)

(*) Spectrochemical analyses by O. JOENSUU. Limit of error is ± 10 % of amount present.
(**) According to upper curve of fig. 2.

prepared by weighing and mixing known amounts of materials. The data relative to these materials are found in table II.

The data of table II are plotted in fig. 2. The agreement of these points with the deduced curve of fig. 2 may be fortuitous. Inasmuch as two different phases were heated in intimate contact, the alkali interdiffusion may not be expected to produce precisely the same Na-K ratio in the two phases. An "equilibrium" distribution of alkali may be developed between the two phases as a function of temperature and of the state of the two phases. No attempt was made to determine the distribution coefficients between the glasses and the crystals; earlier work (LAVES, 1952, p. 567, and unpublished data) on cryptoperthites with K: Na ratios of approximately 1: 1 would indicate that the difference in alkali ratios in the case of "orthoclase" and exsolved albite is approximately 0.1 at 1050°C. The situation is further complicated by the fact that the NaAlSi$_3$O$_8$ glass in the mixtures was observed to be devitrified after thermal treatment; the KAlSi$_3$O$_8$ glass apparently was not. If the distribution coefficient of alkalis between the several phases is near unity, the proposed curve can be considered to be valid. Deviation of the distribution coefficient from unity might move the real positions of the plotted points so that the K-rich materials move to the left, the Na-rich to the right, producing an approach to a straight line relationship.

Additional experiments on a microcline perthite and an albite-microcline anti-perthite were also carried out. Cleavage fragments of a microcline perthite from Pellotsalo (see GOLDSMITH and LAVES, 1954 b) were heated for 15 months at 800°C, with fragments being removed from the furnace periodically during this time. This material, to be discussed in more detail with respect to single-crystal work, was found to be

essentially completely homogenized in the 15 months period. An X-ray powder photograph showed only one phase, but the (400) reflection was somewhat broadened, indicating some internal variation in Na-content. The albite-microcline antiperthite is from an unusual syenitic rock in central Wisconsin. Porphyroblastic feldspar crystals and the main groundmass of the rock are both composed of micro antiperthite with microcline lamellae up to approximately 0.05 mm thickness. This material was heated for four days at 1000°C, and was also observed to be essentially homogenized. Data on these samples are presented in Table III, and plotted as squares on Fig. 2.

THE D$_{(400)}$ DIFFERENCE BETWEEN HIGH- AND LOW-TEMPERATURE K-RICH FELDSPARS.

The separation of the two curves in Fig. 2 has been referred to in terms of a triclinicity difference. It is now quite apparent that the triclinicity of microcline is related to the degree of Al-Si order (GOLDSMITH and LAVES, 1954 b, BAILEY and TAYLOR 1955). It has also been suggested however that many "monoclinic" K-feldspars ("orthoclases") may have a considerable degree of Al-Si order (GOLDSMITH and LAVES, 1954 b). On this basis the separation of the two curves, at least at the K-rich end, might be interpreted more rigorously as a function of both triclinicity and degree of Al-Si order as some order may be present in monoclinic (6) materials. In general, analogous order-disorder relations are expected in the Na-rich portion of Fig. 2.

(6) BARTH (1934) suggested that there were two truly monoclinic modifications of K-feldspar, sanidine and adularia (covered by the term orthoclase). Sanidine was considered

The lower curve of Fig. 2, derived from the data of DONNAY and DONNAY (1952), is for high-temperature and probably highly disordered feldspars. Most monoclinic or apparently monoclinic natural K-feldspars show some change on heating [see COLE, SÖRUM and KENNARD (1949), and COOMBS (1954) for X-ray and optical data, and SPENCER (1937), TUTTLE (1952) for optical data], and thus might not be expected to have had as high a degree of disorder as the synthetic materials. Thus any natural, apparently monoclinic K-rich feldspar could represent a state of Al-Si order

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to have a random Al/Si distribution, and adularia some other Al/Si arrangement. He wrote: «It is a matter of course that the interrelation of the silicon and aluminum atoms has to be such as to correspond to a monoclinic symmetry both in adularia and in sanidine. This is of course geometrically possible, but no data are available through which to suggest any actual arrangement».

Apparently not aware of BARTH's suggestion, CHAO, HARGREAVES and TAYLOR (1940) investigated an orthoclase —an adularia in the terminology of BARTH. They also concluded that sanidine has a random Al/Si distribution, and that the distribution in orthoclase is $4Al + 4Si$ in the Si_1-position, and $8Si$ in the Si_2-position. This conclusion was however withdrawn by Cole, Sörum and KENNARD (1949) who pointed out that the X-ray evidence in the 1940 work was not refined enough to permit such conclusions. However, it was stated that the difference between orthoclase and sanidine may be such as suggested by CHAO, HARGREAVES and TAYLOR (1940), i.e. by BARTH (1934).

Based on BARTH's hypothesis LAVES (1950, Table I) listed the six main Al/Si distributions theoretically possible within the framework of TAYLOR's (1953) structure determination and plausible under the assumption that K-feldspar is holohedral (either monoclinic or triclinic). He stressed (1952, p. 449) the point that the two main monoclinic cases, 1. the one with maximum theoretical disorder: $(2Al + 6Si) + (2Al + 6Si)$ and 2. the one with theoretical maximum order: $(4Al + 4Si) + (8Si)$ could have continuous variation between them and would, therefore, not need a different name. A distinction between sanidine (high) and sanidine (low) with a continuous sequence of intermediate members was proposed.

HAFNER and LAVES (1957) pointed out that it would be highly improbable that the *theoretically* maximum ordered monoclinic case of $(8Si) + (4Al + 4Si)$ would ever be found. This material would have the probability-values $a = 0,00$ and $b = 0.50$, these values giving the probability of finding Al in the corresponding lattice complexes. Taking into account the work of BAILEY and TAYLOR (1955) on an intermediate microcline, HAFNER and LAVES deduced the values $a \approx 0.11$ and $b \approx 0.39$ for what might be called the *actual* case of maximum monoclinic ordering. These values may be compared with the corresponding values of 0.19 and 0.30 reported for orthoclase by JONES and TAYLOR (1961, this volume).

In summing up the variable nomenclature of the truly monoclinic K-feldspars, BARTH's (1934) orthoclase is either sanidine or adularia. Although his sanidine corresponds to CHAO, HARGREAVES and TAYLOR's (1940) sanidine, his adularia corresponds to CHAO, HARGREAVES and TAYLOR's orthoclase. LAVES (1952) calls the sanidine of BARTH and TAYLOR sanidine (high), and the adularia of BARTH and the orthoclase of TAYLOR sanidine (low). For further discussion of the term «orthoclase» the reader is referred to the paper by LAVES and GOLDSMITH (1961, this volume) and to the paper by LAVES (1960) in the case of the term «adularia».

that would place it somewhere between the two curves of Fig. 2.

Nine K-rich feldspars were subjected to severe heat-treatment to further evaluate this effect. In particular the effect of thermal state or degree of order on the composition-sensitive a-axis spacing must be known. The specimens were carefully selected as examples of homogeneous, single phase feldspars, to avoid composition change produced by homogenization of unmixed or zoned material. A variety of structural types were represented, ranging from fully triclinic microcline to sanidine. Small fragments were heated at 1050° - 1060°C for 160 days, and a split of the material was analyzed spectroscopically. The data relative to these samples are presented in Table IV.

A small change in the a-axis spacing is observed in two of the heated monoclinic samples. Similar effects were observed in orthoclases by COLE, SÖRUM and KENNARD (1949), and COOMBS (1954). In the Ft. Bayard orthoclase this change amounts to approximately one-third of the distance between the curves of Fig. 2. It would be desirable to investigate a larger number of "orthoclases" to see what the maximum spacing change in the monoclinic materials might be. Unless one is dealing with a definitely triclinic microcline, it would appear safer to sanidinize the "monoclinic" material before using a determinative curve that is a function of an axial length. It would also be desirable to know the lattice constant differences between "high-temperature" sanidine and "low-temperature" sanidine (TUTTLE, 1952).

The change in b-axis spacing produced by severe heat-treatment is also included in Table IV, in terms of $d_{(010)}$. In going from triclinic microcline to monoclinic sanidine, both b and c change considerably more than a, the change in c being a contraction. The same trend is observed in sanidinized orthoclase (COLE, SÖRUM and KENNARD, 1949), and in the change from albite to analbite (LAVES, 1952). The value of $d_{(010)}$ is more expressive of a change in state than is the change in $d_{(400)}$.

It should be noted that two of the specimens in Table IV did not reach a high-temperature equilibrium state. The authigenic microcline from Pennsylvania (with an initial triclinicity somewhat below the maximum value) was observed to have somewhat diffuse (130) and (131) reflections after heating, indicating residual triclinic geometry. The authigenic microcline from the Kona dolomite is the most recalcitrant feldspar the authors have yet encountered. Heating for 160 days at 1050° - 1060°C produced a triclinicity change of only 10 percent. Similar resistance to thermal change might be characteristic of certain orthoclase-like materials, but would be more difficult to interpret because of initial monoclinic or near-monoclinic symmetry.

TABLE IV

DATA ON SINGLE-PHASE ALKALI FELDSPARS HEATED AT 1050°C, 160 DAYS

Type of Feldspar	Locality	Original triclinicity Δ[1]	Δ of Heated Sample	Spectrochemical Analysis[2]				$\Delta d (400)$[3] Original Sample	$\Delta d (400)$[3] after heating	Absolute change in $d (400)$	Change in $d (010)$
				K_2O	Na_2O	CaO	BaO				
Adularia	Binnenthal Switzerland	$\sim$0; (131) diffuse	0 (131) sharp	15.7	0.38	0.05	0.1	—.0047	—.0047	—	.025$_2$
'Glassy coating' pegmatite[4]	Pala, Calf.	0	0	13.8	1.15	0.24	0.07	.0008	.0000	—.0008	.061$_8$
Orthoclase	Ft. Bayard N. Mex.	0	0	9.8	3.9	0.54	0.95	.0214	.0198	—.0016	.012$_0$
Orthoclase (sanidine ?)	Kokomo, Col.	0	0	11.8	2.3	0.52	1.6	.0125	.0125	—	.006$_0$
Sanidine	Puy de Dome, France	0	0	8.9	4.8	0.55	0.45	.0392	.0392	—	.006$_6$
Authigenic microcline[5]	Stonehenge Pa.	.79	$\sim$0; (131) slightly diffuse	15.5	0.17	0.10	0.08	—.0016	—.0032	—.0016 not equilibrium	.055$_8$
Authigenic microcline[6]	Kona Dolomite, N. Michigan	.97	.87	16.2	0.19	0.17	0.13	.0000	—.0016	—.0016 not equilibrium	.018$_6$
'Adularia'[7]	Near Hot Springs, Ark.	$\sim$0; (131) diffuse	0 (131) sharp	15.8	0.2	⟨0.1	0.35	—.0048	—.0048	—	.031$_2$
'Chesterlite' (microcline)[8]	Chester Co. Pa.	.78	0	16.0	0.45	⟨0.1	0.24	.0010	—.0015	—.0025	0.55$_8$

[1] $\Delta = 1$ for fully triclinic microcline, $= 0$ for monoclinic material, as determined from (131) and (1$\bar{3}$1) reflections, where $\Delta = 12.5 [d_{(131)} - d_{(1\bar{3}1)}]$

[2] Analyses by O. JOENSUU. Limit of error is $\pm 10\%$ of amount present.

[3] Values relative to the Swiss microcline standard. A (—) Δ d signifies an axial length larger than the standard.

[4] Spec. No. 3 in LAVES and GOLDSMITH (1954 b, p. 107). Mislabled No. 13 in Fig. 11.

[5] See BASKIN (1956), Spec. InF.

[6] Ibid, Spec. MK.

[7] Spec. No. 11, GOLDSMITH and LAVES (1954 b, p. 107).

[8] Spec. No. 12, Ibid.

LATTICE ANGLES OF THE MICROCLINE-ALBITE SERIES

In the series of experiments in which powdered microcline and $NaAlSi_3O_8$ glass were heated to produce Na-containing microclines it was noted that the separation of the (131) and (1$\bar{3}$1) reflections, used as a convenient measure of triclinicity (Δ) of microcline, was only moderately affected (7). In addition, 6 microcline perthites from different localities were heated

(7) Although triclinicity was defined in terms of Na-free material (see GOLDSMITH and LAVES, 1954 b).

at 800°C for at least one month, and one at 1050°C for 3 days with similar results, although several of the microclines took up to 25 percent $NaAlSi_3O_8$ in solid solution near albite lamellae. If one assumes a linear change in lattice angles between the end members microcline and albite, the separation of the (131) and (1$\bar{3}$1) reflections should have been affected much more than was observed from the powder patterns.

To clarify this situation, single-crystal X-ray work was done on several members of the microcline-albite series, with introduced $NaAlSi_3O_8$ contents of approximately 26, 62 and 90 percent. These materials were:

1) The microcline perthite from Pellotsalo with

TABLE V

SINGLE-CRYSTAL DATA [1] ON MICROCLINE-ALBITE SOLID SOLUTIONS

Sample	$NaAlSi_3O_8$ Content	$d_{(100)} = 1/a^*$	α^*	β	γ^*	$010/\overline{1}01$
Untreated Microcline [2]		7.70₇	90°25′	115°56′	92°16′	88°40′
Pellotsalo	26 %	7.63₇	90°18′	115°53′	92°12′	88°16′
Wisconsin	62 %	7.46₈	88°18′	116°17′	90°57′	87°18′
Swiss Crystals, removed from matrix	~90 %	7.32₂	87°15′	116°47′	not measurable	86°31′
Albite [3]	~100 %	7.29₉	86°22′	116°40′	90°30′	85°57′

[1] Buerger precession technique used.
[2] Hybla, Ontario: Data from LAVES (1952).
[3] Data from LAVES (1952).

untwinned microcline (GOLDSMITH and LAVES, 1954 b) heated for 15 months at 800°C. The unheated microcline is fully triclinic, and $d_{(400)}$ is the same as the Swiss microcline. Single crystal pictures of the unheated perthitic albite show it to be the normal low-temperature modification, with approximately 3–5 percent An in solid solution, on the basis of its lattice angles (LAVES 1954).

2) The albite-microcline anti-perthite from Wisconsin, heated for 4 days at 1000°C. The unheated microcline is fully triclinic or nearly so, with $d_{(400)}$ the same as the Swiss microcline. The albite is the normal low-temperature modification without significant anorthite.

3) Crystals of the Swiss authigenic microcline embedded in powdered $NaAlSi_3O_8$ glass (approximately 90 percent of the mixture was glass), and heated for 17 days at 800°C. The crystals were approximately 0.1 mm in their largest dimension.

The heat treatment of these materials produced an essentially homogeneous product in terms of composition. The time required for homogenization of the different samples was determined by means of repeated optical and X-ray checks. The compositions of the first two materials are show in Table III. The composition of the third material was determined by its (400) spacing from single-crystal pictures. Data on these crystals are presented in Table V, and plotted in Fig. 3.
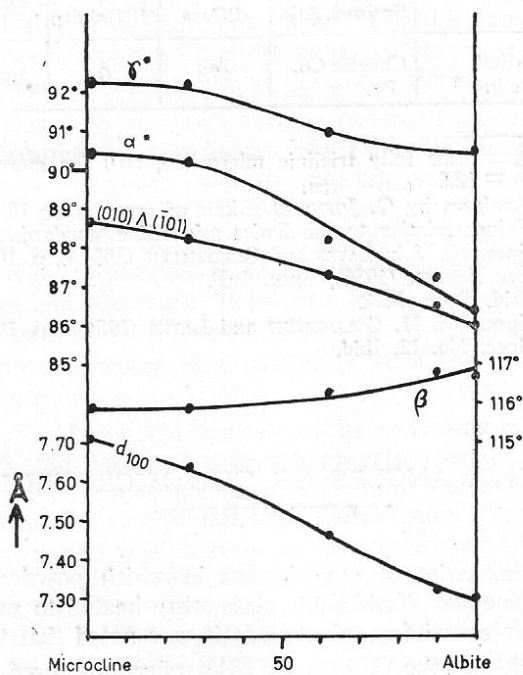
Fig. 3.—Single-crystal data on microcline-albite series (see Table V).

The data of Table V and Fig. 3, although meager, clearly show that the relationship between lattice angles and composition is nonlinear. In fact, α^* and

γ^* are changed only slightly in Na-microclines with compositions up to 25-30 percent $NaAlSi_3O_8$. If one neglects axial lengths, it is these angles that control the separation of the $(1\bar{3}1)$ and (131) reflections. Thus one would not expect much change in the apparent triclinicity (see footnote 7) of microclines that contain up to 25-30 percent $NaAlSi_3O_8$ (8). The apparent triclinicity of the homogenized Pellotsalo microcline with 26 percent $NaAlSi_3O_8$ was observed from powder data to be 0.87, and the heated mixtures of 75 percent Swiss microcline and 25 percent $NaAlSi_3O_8$ glass earlier described showed values of slightly over 0.8.

EVIDENCE FOR THE COMPLETE SERIES BETWEEN MICROCLINE AND ALBITE

Evidence for the series of solid solutions between microcline and albite has been given by LAVES (1951, 1952). Additional data relating to the complete nature of this series are presented here.

1) Seven microcline perthites from various localities were heated at 800°C for times ranging from 7 to 31 days. The following $NaAlSi_3O_8$ contents were determined from powder photographs of the variously treated materials, using Fig. 2: 5 percent, 8 percent, 10 percent, 2 values of 16 percent, 2 values of 17 percent, 19 percent. One specimen showed a continuous range from 12 to 25 percent. In addition, a number of samples showed large gradations in composition and could not be accurately measured.

2) Powder work on the mixtures of Swiss microcline and $NaAlSi_3O_8$ glass show solutions in the same range as 1) above, and in addition, a mix of 50 percent microcline and 50 percent glass produced a range of material from 44 to 53 percent $NaAlSi_3O_8$ (see Table II).

3) Three mixtures of microcline crystals and powdered $NaAlSi_3O_8$ glass were heated at 850°C for two days. A short heat-treatment was used to produce compositional gradients in the crystals. Two of the mixtures consisted of fragment ($\sim 0.1mm$) of microcline from Hybla, Ontario, and of the untwinned Pellotsalo material; the other contained Swiss authigenic crystals. All three samples were examined optically and by the Buerger precession method, and results were essentially the same in all cases. Gradational extinction angles on (001) of the order of ten degrees were observed from the centers to the edges of the crystals. Gradations in composition are best

shown by the (400) reflections in c-axis precession pictures. As an example, measurements were made on a Pellotsalo fragment; reflections from a K-rich material were connected to those of a Na-rich material by a continuous streak, representing a continuous range of compositions within a single untwinned crystal. Measurement of the K- and Na-rich extremes showed a compositional range from 31 to 88 percent $NaAlSi_3O_8$.

4) Fragments of the albite-microcline anti-perthite from Wisconsin were heated for 3 days at 850°C, for 1 day at 1000°C, and for 4 days at 1000°C. Precession photographs of a fragment from the 850°C heat-treatment showed reflections from the original microcline and albite with weak and diffuse connections. In 1 day at 1000°C, none of the original microcline or albite remains, but somewhat diffuse reflections indicate a range of compositions between approximately 45 percent and 75 percent $NaAlSi_3O_8$. As discussed earlier the material was essentially homogeneous after 4 days at 1000°C. Essentially similar gradations of composition were observed in fragments adjacent to albite lamellae removed from heated pieces of the Pellotsalo microcline.

These observations, coupled with the data of the previous sections, clearly show that the complete range of compositions between microcline and albite can be attained.

THE RELATION OF THE MICROCLINE-ALBITE SERIES TO THE EQUILIBRIUM DIAGRAM OF THE ALKALI FELDSPARS

All of the artificially prepared members of the highly ordered microcline-albite series were made at temperatures that are unquestionably above the range
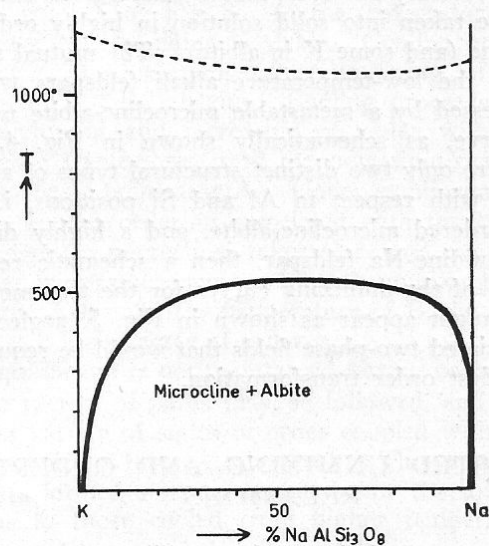
Fig. 4.—Schematic metastable microcline-albite unmixing curve.

(8) MACKENZIE and SMITH (1955) discuss observations on heated specimen N and state, «The angles of the triclinic potash phase do not change directly toward low-temperature albite as would be expected if complete solid solution exists between microcline and low-temperature albite (LAVES, 1952)». This objection is not valid on the basis of the evidence presented here.

in which the low-temperature alkali feldspars are stable. Thus all of these materials represent metastable solid solutions in the temperature range (800°C and above) at which they were prepared; this range lies in fields of the highly disordered feldspars. The metastable preservations of high-temperature states at low temperatures is well known, particularly in the feldspars, and lattice constants have been measured at room temperature on the phases stable at high temperature
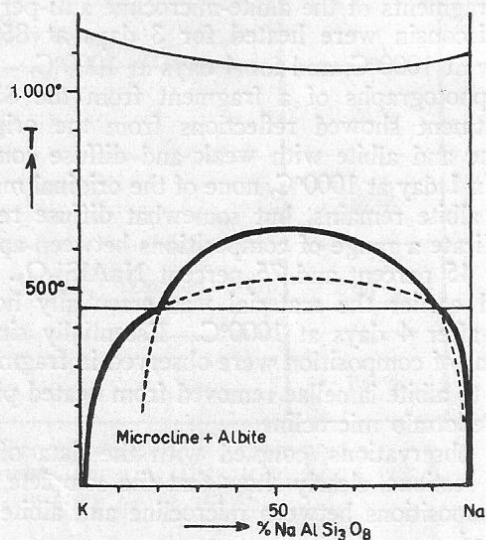
Fig. 5.—Schematic representation of the unmixing curves of highly ordered and highly disordered alkali feldspars. The upper curve corresponds to that determined by BOWEN & TUTTLE (1950). Associated two-phase fields are neglected.

(DONNAY and DONNAY, 1952). The reverse situation, or superheating of the microcline-albite series, is just as real.

It is necessary however, that at least a small amount of Na be taken into solid solution in highly ordered microcline (and some K in albite). The mutual solubility of the low-temperature alkali feldspars would be expressed by a metastable microcline-albite unmixing curve, as schematically shown in Fig. 4. If there were only two distinct structural types of alkali feldspar with respect to Al and Si positions, i.e. a highly ordered microcline-albite, and a highly disordered sanidine-Na feldspar, then a schematic representation of the unmixing curves for the two modifications might appear as shown in Fig. 5, neglecting the associated two-phase fields that would be required for the first order transformation.

SUGGESTED UNMIXING AND ORDERING RELATIONS

If it is assumed that under equilibrium conditions the degree of order is a continuous function of temperature, any intermediate state of order that is attained

would be associated with a solvus that is characteristic of that particular state. Thus a whole family of curves should exist in positions intermediate between the low-temperature microcline-albite solvus and the high-temperature solvus. However, none of these curves can be an equilibrium solvus, and only two points (one K-rich, the other Na-rich and at different temperatures) on any of the curves can coincidentally approach points on the equilibrium solvus. This is because the solvus is a polythermal curve, and under equilibrium conditions, if the degree of order changes with temperature, a new set of solvus points for the new temperature and degree of order (in principle different on the K- and Na-sides) become stable. Thus intersections do not represent stable points of coincidence with the equilibrium solvus in terms of either solubility or degree of order. The stable solvus approximates an envelope of all metastable solvus curves, assuming the topological relations between the solvus curves of the high- and low-temperature series are as depicted by LAVES (1952, Fig. 10A, p. 559) (9). These relations are shown diagrammatically in Fig. 6; the Na- rich end of the diagram, where the relations may in principle be the same, is not considered.

However, there is some evidence that at the tem-
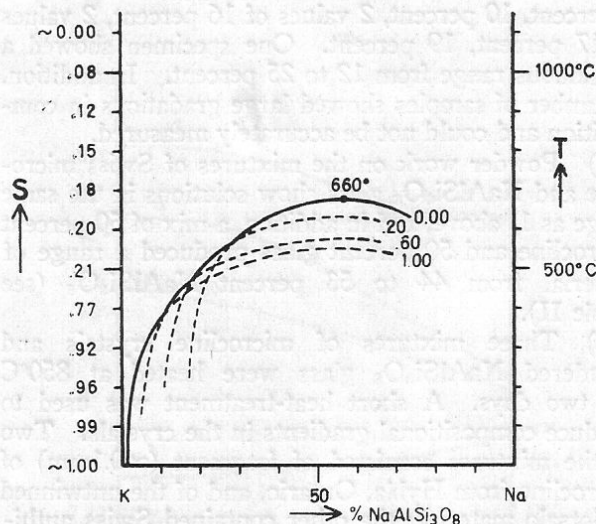
Fig. 6.—Diagrammatic representation of several of the infinite family of curves representing effect of degree of order on unmixing. The envelope of these metastable curves approaches the equilibrium solvus with a reservation discussed in the text and shown in Fig. 8. The curve of degree of order = 0 is from BOWEN & TUTTLE (1950).

(9) Although there are no direct experimental data on the solubility-temperature relations in the microcline-albite series, there is some evidence that the crest of the solvus is at a lower temperature than the crest of the solvus in the high-temperature alkali feldspar series as determined by BOWEN & TUTTLE (1950). This point is discussed and evidence on the homogenization of a moonstone is given by LAVES (1952, pp. 558-559).

peratures of the top of the uppermost solvus shown, some Al-Si order exists *under equilibrium conditions* (see for example LAVES, 1952, p. 558). Earlier publications by GOLDSMITH and LAVES (1954 a, b) considered a continuous change of order in the triclinic state only, and for convenience set the degree of order equal to zero at the triclinic-monoclinic transformation. If it is considered that Al-Si disorder is not complete at this transformation temperature, but may be approached near the melting point, the relations would be as shown schematically in Fig. 7. This figure was constructed from the relation $S = \dfrac{p-r}{1-r}$

(see for example BARRETT, 1952, p. 275) (10).
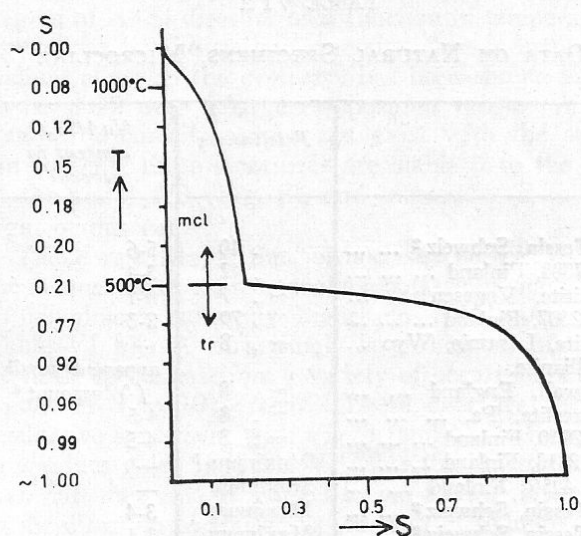
Fig. 7.—Schematic long-range order versus temperature diagram for KAlSi₃O₈. The triclinic-monoclinic transformation is shown at 500° (GOLDSMITH & LAVES, 1954 a). For further details see text and foot-note 10.

Let us arbitrarily assume (in accordance with fig. 7) that at 660°, at the top of the solvus determined by BOWEN and TUTTLE (1950), a degree of order of approximately 0.2 exists under equilibrium conditions. Then, it would be required that *under equilibrium conditions* the uppermost solvus (being valid only for a material of S approximately = 0) of Fig. 6 would not be realized, but that the stable solvus for the appro-

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(10) In this formula r is the fraction of the available sites occupied by the «right» atoms at perfect order, i.e. r = 0.25 in the case of AlSi₃ when the order of Al is considered; p is the probability of a «right» atom occupying the «right site», i.e. the values b and b₂ as derived by LAVES (1960, fig. 5, p. 273). It should be stressed that these values (b and b₂) used in constructing fig. 7 have not been experimentally determined, and figures 6-8 merely represent a (plausible) attempt to topologically illustrate the ordering and unmixing relations as a function of temperature, in accordance with considerations of structural theory and of experimental evidence from several sources.

priate degree of order, lying at somewhat lower temperature, would be the effective one.

Under these conditions, the equilibrium relations are shown diagrammatically in Fig. 8. In this figure a degree of order varying with temperature has
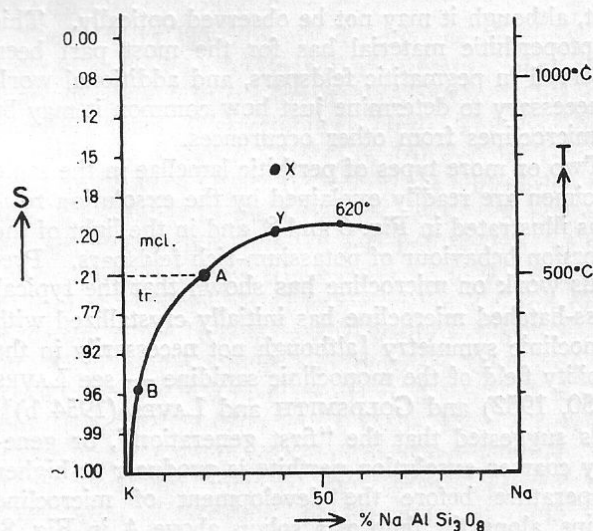
Fig. 8.—Diagrammatic representation of the exsolution relations under equilibrium conditions.

been crudely assigned, as in Fig. 7, and is shown at the left of the diagram. Triclinic materials are arbitrarily shown as having a degree of order greater than 0.21. Thus an effect of disorder on the solid-solubility of monoclinic states is shown as well as that on the triclinic materials. In Fig. 6 only several of an infinite family of curves are shown in order to illustrate the principles.

Let us consider the *equilibrium* cooling of a feldspar at point X on Fig. 8. At the temperature of X a homogeneous sanidine is stable. Cooling proceeds to point Y, at which temperature unmixing (of a material with S ≈ 0.2) begins. Cooling proceeds along with unmixing and increasing of order within the monoclinic framework, until the potassium-rich feldspar reaches a point near A. Under equilibrium conditions, further ordering associated with the symmetry change (to microcline) takes place and the degree of order increases concurrently with unmixing along the curve A-B. At the temperature of B, the microcline has a high degree of order.

If equilibrium is not maintained during cooling, an infinite variety of paths may be followed, and a fascinating variety of states of order coupled with a varied exsolution history can result. This applies to feldspars formed at temperatures below the solvus as well as to those cooled from higher temperatures. The great diversity of the alkali feldspars is a consequence of the difficulty of attaining equilibrium in this system.

Many microclines show two types of perthitic lamellae, one much finer than the other (see for example ANDERSEN, 1928, on film and vein perthite, etc.). The writers have also noted that X-ray photographs of small regions between the visible perthitic lamellae of many microclines commonly show albite to be present, although it may not be observed optically. This cryptoperthitic material has for the most part been observed in pegmatitic feldspars, and additional work is necessary to determine just how common it may be in microclines from other occurences.

Two or more types of perthitic lamellae in the same specimen are readily explained by the exsolution relations illustrated in Fig. 6 and 8, and in the light of the inversion behaviour of potassium-rich feldspars. Previous work on microcline has shown that the typical cross-hatched microcline has initially crystallized with monoclinic symmetry [although not necessarily in the stability field of the monoclinic sanidine — see LAVES (1950, 1952) and GOLDSMITH and LAVES (1954 b)]. It is suggested that the "first generation", or generally coarser exsolution perthite is producer at higher temperature before the development of microcline begins, along the limb of a solvus above A in Fig. 8. The finer or cryptoperthitic albite can be produced in several ways; let us consider two "extreme" situations. In both cases it is exsolved as a consequence of increased ordering after the development of triclinic material has begun; in the first case during equilibrium inversion following curve A-B (Fig. 8), the finer lamellae being a result of the decreased ionic mobility at lower temperatures. The other extreme is produced by non-equilibrium cooling, with the exsolution path following a metastable extension (cf. Fig. 6) of a solvus of a more disordered state below A. If ordering begins at lower temperatures after undercooling, as is quite likely in the exceedingly sluggish alkali feldspars, a second generation of finely divided albite could be exsolved when the microcline was ultimately developed. In the final or highly ordered microcline, a rather pure phase expressed by the downward continuation of the stable solvus below B would be produced. [For additional experimental data on the orientation relations between microcline and albite in perthites see LAVES and SOLDATOS (1961)].

DISCUSSION OF NATURAL SPECIMENS

X-ray powder photographs of over 100 selected specimens of perthitic potassium-rich feldspars have been taken to evaluate the sodium content of the potassium-rich phases. Most of the specimens were microcline, some with intermediate values of triclinicity. A smaller number were "orthoclase" perthites, although many showed fuzzy or somewhat diffuse (130) and (131) reflections, indicating some material of low

triclinicity. A selection of the specimens is presented in Table VI a and b, with data on triclinicity and the amount of $NaAlSi_3O_8$ in solid solution.

It is apparent that microclines contain very little $NaAlSi_3O_8$ in solid solution. The highly ordered microclines contain less than 5 percent. There is some indication that the intermediate microclines have slightly more $NaAlSi_3O_8$ than those with maximum triclinicity. This would fit our interpretation as expressed in Fig. 8. However, the values for the intermediate microclines in Table VI a were determined by choosing an appropriate curve between the two curves of Fig. 2, as a triclinicity correction; this may

TABLE VI a

DATA ON NATURAL SPECIMENS, MICROCLINE

	Triclinicity (Δ)	$NaAlSi_3O_8$ content in percent [1]
θ_3, Tessin, Schweiz [2]	. 40	5-6
GF 7888, Finland	. 42	3-4
Granitite, Vogesen	~ . 7	0-1
AK 2307, Finland	. 79	2-3
Syenite, Laramie, Wyo ...	~ . 8	—[3]
Luxillianite, Cornwall, England	~ . 8	apparent small, (-) amount [4]
Chesterlite, Pa.	~ . 8	4-5
No. 2910, Finland	~ . 8	4-5
AK 2313, Finland	Maximum [5]	—
SM 4056, Finland	Maximum	—
B₃, Tessin, Schweiz [2]	Maximum	3-4
B₅, Tessin, Schweiz [2]	Maximum	3-4
Pellotsalo, untwinned	Maximum	—
AK 2316, Finland	Maximum	—
Graphic Granite, locality unknown	Maximum	2-3
Granulite pegmatite, Finland	Maximum	2-3
Felch, Michigan	Maximum	3
Granite porphyry, Worcester, Mass.	Maximum	—
Granite, Leadville, Col. ...	Maximum	3-4
Kluntarna, Sweden	Maximum	(-) amount [6]
Granite, Platte, Canyon, Col.	Maximum	apparent small, (-) amount [7]
Amph. granite, Vogesen ...	0 to near Max	8 to —

[1] From Fig. 2, corrected for Δ. Several microclines with $d_{(400)}$ giving apparent (-) values of sodium have been noted. Analyses of these materials have shown rather high $Rb_2O \pm BaO$ contents. The larger size of the Rb^+ ions apparently produces the cell expansions observed.

[2] See Paraskevopoulos (1953), and GOLDSMITH and LAVES (1954 b, p. 115).

[3] — Indicates same spacing as Swiss standard; (-) indicates «negative» value.

[4] Spectrochemical analysis shows $Na_2O \sim 0.3$; $K_2O \sim 16.3$; $Rb_2O \sim 0.3$; $BaO \sim 0.1$.

[5] Maximum triclinicity is approximately 0.95.

[6] Contains 1.85 % Rb_2O.

[7] $Na_2O \sim 1.9$ (seen as exsolved albite); $K_2O \sim 14.6$; $Rb_2O \sim 0.6$; $BaO \sim 1.2$.

be subject to an error of approximately ± 2 percent $NaAlSi_3O_8$. Nevertheless, even the intermediate microclines are quite low in sodium. These data show fairly conclusively that the microcline solvus approaches the pure $KAlSi_3O_8$ border of the phase diagram with decreasing temperature, i.e., that exsolution is virtually complete at room temperature.

MacKenzie (1954, p. 364) has stated that "It seems possible that variations in the lattice of microclines might be directly related to their chemical composition, as has been shown to be the case in the anorthoclase series (Donnay and Donnay, 1952)". The data presented here and by Goldsmith and Laves (1954 a, b) show that this comparison is not valid. The triclinicity under equilibrium conditions is influenced by the degree of Al-Si disorder as a function of temperature as well as by the sodium content. The influence of sodium alone on the *geometry* has been shown above to be small over a large composition range. A variety of triclinicity values can exist with the same Na content; these structures are stable if to the left of the curve AB (Fig. 8), and metastable if to the right of this curve.

The X-ray data on the "orthoclase" perthites show the monoclinic or near-monoclinic potassium-rich phase to be almost uniformly higher in $NaAlSi_3O_8$ (see Table VI b). A surprisingly large number of these perthitic specimens from a variety of occurrences give values of 8 to 10 percent. These data are also in qualitative agreement with Fig. 8 (and 6). The absolute values given in Table VI b for the "monoclinic" materials may also be subject to some error, however, in the direction of appearing too high in sodium. As earlier described, sanidinization of some apparently

monoclinic potassium feldspars produces a shift of $d_{(400)}$ in the direction of apparent lower sodium content. Unfortunately sanidinization of perthitic material (as a check on composition) is difficult, as perthite-free portions must be used to avoid adding $NaAlSi_3O_8$.

The writers have observed only one specimen of triclinic potassium feldspar that contains more than approximately 5 to 6 percent $NaAlSi_3O_8$. This specimen is from Jekaterinburg, Urals, and has been described by Böggild (1924, p. 16) and by Goldsmith and Laves (1954 b); Böggild's optical description is reprinted in the latter reference. X-ray precession photographs of small selected portions of this unusual material show triclinicities up to 0.8 although most of the material is of lower triclinicity, and parts bordering albite lamellae are virtually monoclinic. A variety of single-crystal and powder X-ray measurements on the intermediate material (up to $\Delta = 0.8$) show the $NaAlSi_3O_8$ content to be 13 ± 2 percent. Interestingly enough, several measurements on the nearly monoclinic material show several percent less $NaAlSi_3O_8$. Precession photographs of both the "monoclinic" and triclinic portions show a few percent of cryptoperthitic albite, but less is present in the triclinic portions. This sample might represent an example of a naturally reheated material.

APPENDIX I

Some Observations on the Homogenization of Alkali Feldspars.

Comparison of thin sections cut from the Pellotsalo microcline perthite before and after heat-treatment (15 months at 800°C) is of interest. The original material is predominantly a large single crystal of microcline, with but few small regions that are twinned (see Laves and Goldsmith, 1954 b, Fig. 15 a). Albite veins up to approximately 0.5 mm in thickness are interfingered with the single-crystal microcline. Albite twinning is present in the albite veins. Fig. 9 A is a schematic sketch of this original material. The extinction angle of the microcline on (001) and against (010) is $+ 18°$, the albite is $- 4°$. In the thin section of the heated material the borders of the veins have disappeared; the section is schematically drawn in Fig. 9 B. The entire section is now compositionally homogeneous. The set of albite twin lamellae that had the same $AlSi_3O_8$ framework orientation as the microcline (set A in Fig. 9 A) has coalesced with the microcline, and only the other twin set remains visible in polarized light. The extinction angle of the Na-containing microcline dropped to $+ 10°$.

Several of the thicker albite lamellae retain central "stringers" of unaltered original albite. The border

Table VI b

Data on Natural Specimens, Orthoclase

SAMPLES

	Triclinicity (Δ)	$NaAlSi_3O_8$ content in percent [1]
Pegmatite, Pala, Cal.	0	13
$\pm$ 2964 granulite, Finland ...	near 0	8 — 9
GF 7888, Finland (monoclinic portion)	0	8 — 9
$\pm$ 7922 granulite, Finland ...	near 0	8 — 9
GF 3077 Rapakivi, Finland ...	range near 0	8 — 9
A₇, Tessin [2]	range near 0	6 — 7
Granite, Ellicott Cty.	range near 0	9 — 10
Granite, Weinheim, Baden ...	0	10
Granitite, Vogesen	0	10
GF 5437 Rapakivi, Finland ...	near 0	9

[1] From Fig. 2.
[2] See Paraskevopoulos (1953), and Goldsmith and Laves (1954 b, p. 115).
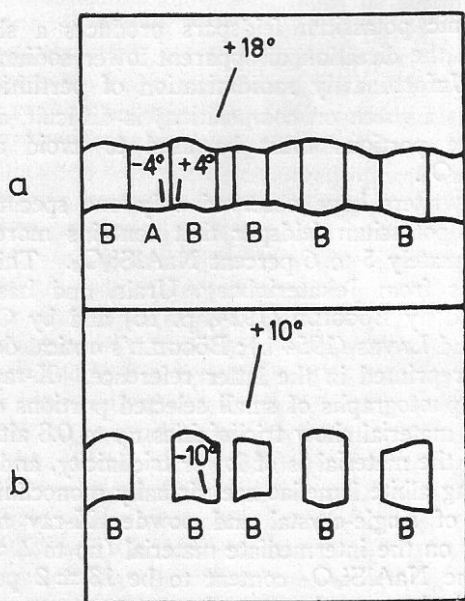
Fig. 9.—A) Diagrammatic sketch of thin section parallel (001) of Pellotsalo microcline perthite before heat-treatment (see Appendix I) showing an albite vein, twinned after albite law.

B) Diagrammatic sketch of thin section of Pellotsalo microcline after heat-treatment.

Extinction directions are indicated.

between the homogenized portions of the lamellae and the pure albite remnants is fairly sharp. No analogous remnants of pure microcline were observed in the portions of the crystal that were originally single-crystal microcline (11). It is apparent that the rate of diffusion of Na^+ within microcline at 800°C is greater than that of K^+ within albite. This might be expected on the basis of the difference in size of the two ions.

The same conclusion could also be drawn from the homogenization behaviour of powdered mixtures of several components. A mixture of 50 percent Swiss microcline and 50 percent $NaAlSi_3O_8$ glass had approached homogeneity after 17 days at 800°C (see Table II), but a similarly prepared mixture of 50 percent Amelia albite and 50 percent $KAlSi_3O_8$ glass was far from equilibrium, and had residual albite remaining after the same heat treatment.

APPENDIX II

ADDITIONAL DATA ON THE (400) SPACING OF MICRO-
CLINE AND THE USE OF A SILICON STANDARD.

The spacing values $d_{(400)}$ microcline = 1.930 Å, and albite = 1.824 Å were determined by measuring

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(11) The optical effects consequent upon homogenization are clearly shown in the material because of the lack of cross-hatch twinning.

the spacing difference between these low-temperature forms and their high-temperature polymorphs, using the d-values of the high-temperature forms given by DONNAY and DONNAY (1952), see footnote 2. This was done to clarify the difference in these spacings, and the absolute values ultimately depend on the silicon standard used by DONNAY and DONNAY in their work (see footnote 5) on the high-temperature modifications. For the purposes of this paper, the use of the authigenic microcline as an X-ray standard was most convenient, but it is perhaps desirable to include comparative data obtained with another standard that is readily available.

Silicon is an excellent standard for this purpose as the (220) reflection has a d-spacing of 1.9200 Å (when CuK_{α_1} and CoK_{α_1} is taken as 1.54051 Å and 1.78892 Å), very close to that of $d_{(400)}$ of microcline. Measurements on thirteen films gave an average of — .0072 for the difference between the (400) microcline and (220) silicon spacings. The negative value is used to adhere to the convention used throughout the paper of $d_{(Standard)} - d_{(unknown)} = \Delta d$. This value of Δd gives a value of $d_{(400)}$ microcline = 1.927_2 Å for the pure authigenic material. Re-plotting the ordinate of Fig. 2 can readily be done for use with the silicon standard [the values of the right ordinate of fig. 2 represent the values: $d_{(110)}$ (silicon) — $d_{(400)}$ (unknown)].

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DISCUSSION

J. V. SMITH (Chicago), written comments:

1. SPENCER (1937) described optical effects, visible only under special illumination, that may represent exsolution formed at a stage even earlier than those represented by the perthites described by ANDERSEN, and mentioned by GOLDSMITH and LAVES.

2. The results of Coombs, TUTTLE and others on orthoclase perthites showed that compositions for the two phases determined from $\bar{2}01$ spacings were unreliable and might be in error by 20 %. The reason seems to be that strain forces the two phases to join along the perthite composition plane, producing a correspondingly larger difference in the direction perpendicular to the composition plane. The net effect is to give rougly the same volume for a phase when in a perthite and when alone. It is possible that the same effect occurs in microcline perthites in which case the compositions determined for the separate phases are in error. The direction of the error is such as to give a higher Or content than is actually present. The writer and GOLDSMITH are planning X-ray emission microprobe analyses of perthites in order to determine directly the compositions of perthites and to test the validity of compositions estimated from X-ray spacing measurements.

Because the strain in a perthite occurs only at the contact, the effect should decrease as the lamellae become broader. Consequently, the strain in microcline perthites would tend to be less than in the generally finer orthoclase perthites.

There is a faint possibility that replacement perthites can be distinguished from exsolution perthites by examination of X-ray photographs to determine the strain. In exsolution perthites, strain is inevitable because the lamellae are trapped in each other. In a replacement perthite it is possible that the infiltration of material from outside could lead to structures with less strain. However the possibility that such an effect exists and could be used as test of whether granitization has occurred is thought to be remote. Nevertheless it seems worth a test.

GOLDSMITH (Chicago) and LAVES (Zürich). Answer to point 2:

One of us (F. L.) observed and described in 1952 the fact

that $(\bar{2}01)$ or in general (h00) reflection measurements are unreliable for the determination of chemical compositions (*J. Geol.*, 1952, **60**, p. 562-566), for they lead to values of Ab content which may be too high by as much as 10 % (*). In *Z. Kristallogr.* **107**, (1956) p. 200 Laves pointed out that the lattice constants (a, b, c, α, β, γ, α^* etz.) were unreliable for the characterization of feldspar phases when they are determined from crypto- to micro-perthitic material. We are thus fully aware of the strain-composition effect. It is, however, hard to evaluate this effect quantitatively, for it

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(*) Prof. J. V. Smith (oral communication) states that Tuttle's observation was communicated to him orally, and published in the *G. S. A. Memoir* No. **74** (1958). In addition, the 20 % error he mentions is a «gros» error, of ~ 10 % on both sides of the immiscibility gap.

depends on the size, shape and distribution of the exsolved material, and no systematic study has yet been made. On the other hand we do not believe that the strain effect of the exsolved guest material of a perthite *on the host* will be great if the guest is present only in the amount of say 10 % or less. Thus, this effect will not affect the conclusions drawn in our paper, as we are concerned with the lattice constants of the K-feldspar host on the K-side of the alkali feldspar diagram. Of course, any attempts to determine the amount of exsolved guest material using the intensities of the guest have to take into consideration that such intensities will be affected by the size, shape and structure of the «exsolved» domains and by the strains involved within such arrangements, especially in those that have been classified (Laves, 1952, p. 563) as «quasi-homogeneous perthites», following a term coined by Oftedahl (1948, Norsk. Ak. Oslo, Skr. I, No. 3, p. 67).

The relation between structure and optical orientation in potash-soda feldspars

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ABSTRACT

The X-ray constants of potash feldspars depend upon the degree of disorder and of submicroscopic twinning. It is shown how these factors can be separated by optical means.

Measurements of the orientation of the indicatrix of chemically and X-ray investigated potash-soda feldspars, with improved technique are described. A diagram of the optical orientation of alkali feldspars was constructed. Some petrological conclusions drawn from these data are discussed.

I. INTRODUCTION

During the last twenty years several X-ray methods heve been introduced into the study of structural state of the alkali feldspars. They are as follows: the determination of the mean cation — O distances indicating Al-Si distribution (Chao, Hargreaves and Taylor, 1940), the determination of the triclinicity (Goldsmith and Laves, 1954) and of the reciprocal lattice angles α^* and γ^* (MacKenzie and Smith, 1955).

However, optical variants of the potash feldspars (known for about a century) cannot be completely described by these methods. Measurements of infrared absorption (Hafner and Laves, 1957) show that there is not only a relation of order-disorder in respect to the Al-Si distribution between these variants (Barth, 1934, 1959, Laves, 1950, 1952, Bailey and Taylor, 1955, Megaw, 1959), but also a relation of submicroscopic (sub-X-ray) twinning. The latter corresponds to Mallard's hypothesis (1876) and Ito's X-ray interpretation of some polymorphs (1950). This conclusion cannot be drawn from the X-ray investigations which only show summarized patterns as a result of the changes in the Al-Si distribution and submicroscopic twinning.

The present paper deals with the optical orientation which permits separation of these two factors.

There has not been much investigation of the orientation of the indicatrix in potash-soda feldspars. V. V. Nikitin (1933) proposed a tentative diagramm of optical orientation of potash soda feldspars. D. S. Beljankin (1937, 1944) concluded from Fedorov stage measurements that there is a continuous series of members (in his notation "potash anorthoclases") showing optical symmetry and optic axial angles intermediate between those of triclinic microcline and monoclinic sanidine. D. S. Belyankin (1937)

G. D. Afanasiev (1951), V. P. Petrov (1955) showed a geological significance for the ranges of optical properties of alkali feldspars in magmatic rocks in the Caucasus. L. A. Vardanjanz (1957) proved the necessity for the statistical measurement and treatment for description of optics of potash feldspars in magmatic complexes. With this aim in view V. K. Monich (1952) suggested that a diagram on rectangular coordinates should be used. Without knowledge of these works G. M. Paraskevopoulos (1953) described triclinic orthoclases from Tessiner pegmatites. Using Nikitin's classification and diagram M. Gysin (1957) investigated with the universal stage the range of optical orientation of "triclinic orthoclases" from some rocks of Nepal. Nikitin's diagram was also used by Chr. Oftedahl (1948) for the study of cryptoperthites of the Oslo region and by A. Wilson (1950) who studied unusual optical orientation of some cryptoperthites in Central Australian charnokites (compare the specimens No. 35-36 in Table I of this paper). Optical orientation of the Na-rich sanidines and anorthoclases was determined by O. F. Tuttle (1952). In their investigations E. Spencer (1957) and C. G. Hewlett (1959) measured only extinction angles.

In the present paper only a few published measurements of optical orientation could be incorporated, because only the more precise data could be used. Therefore it was found necessary to make new measurements by an improved technique.

II. EXPERIMENTAL INVESTIGATION

Forty seven specimens (Table I) were selected for this investigation from an original collection of 130 potash-soda feldspars. They include various samples from the main types of magmatic and metamorphic

TABLE I

THE OPTICAL ORIENTATION DATA

Number of spec.	LOCALITY AND ROCKS	Number of slides	− 2 V°	A		B		⊥(010) ∧ Ng	Extinction on (010)
				+ λ	+ φ	+ λ	− φ		
	Sanidines:								
1	Guelkend (Armenian SSR). Paleogene liparite..................	2330	12,0 ∥ (010)	11,5	0,0	0,5	0,0	90,0	5,5
		2330	14,0 ⊥ (010)	5,5	7,0	5,5	7,0	0,0	5,5
2	Dva brata (West Caucasus), eruptive breccia..................	2105	6,0 ∥ (010)	9,0	0,0	3,0	0,0	90,0	6,0
3	Tyrny-Aus I (North Caucasus), Tertiary intrusive liparite.........	2155	18,0	6,8	9,0	6,8	9,0	0,0	6,8
	Na-anorthoclases:								
4	Dariganga I (Mongolia), lava of Quaternary volsans....................	2054	53,0	9,0	26,5	9,0	26,5	0,0	9,0
5	Dariganga II..............................	2053	41,0	6,8	18,0	9,5	23,0	4,2	8,2
	High orthoclases and microclines:								
6	Kluchi (East. Transbaikalien), dyke of hybrid porphyry.....................	2293	39 (43)	6,6	19,5	6,6	19,5	0,0	6,6
		2294	42 (43)	6,5	21,0	6,5	21,0	0,0	6,5
7	Tyrny-Aus II, Tertiary porphyrytic granite	2322	37,5 (43)	5,5	18,75	5,5	18,75	0,0	5,5
		2326	48,0	8,0	24,0	8,0	24,0	0,0	8,0
		2326	52,0	6,0	28,3	9,5	23,5	4,0	7,8
		2328	49,0	7,8	24,5	7,8	24,5	0,0	7,8
		2328	52,0	6,0	28,0	8,0	27,3	2,2	7,0
		2325	55,5	7,8	29,0	8,2	26,5	1,5	8,0
		2323	53,2	6,0	27,8	10,0	25,0	3 8	8,0
		2323	56,0	6,0	30,3	10,3	25,0	4,5	8,1
		2323	59,0	5,0	32,5	10,0	26,3	5,5	7,5
8	Tyrny-Aus III, pegmatite vein in granite..	2051	38,0 (41,0)	6,5	19,0	6,5	19,0	0.0	6,5
9	Tyrny-Aus IV, drusy cavities in granite..	2027	43,0	6,5	21,5	6,5	21,5	0,0	6,5
		2027	56,0	8,5	28,0	8,5	28,0	0,0	8,5
10	Ortotokoi I (Kirghiz SSR), giant-porphyrytic syenit...	2156	49,0	6,0	24,5	6,0	24,5	0,0	6,0
		2154	52,5	6,5	26,3	6,5	26,3	0 0	6,5
11	Ortotokoi II (the same locality)...........	2230	58,0	5,5	29,9	5,5	29,0	0,0	5,5
12	Kukisvumchorr (Kola peninsular), pegmatites of nepheline syenite of Khibine massiv..........................	2179	55,0	6,0	27,5	6,0	27,5	0,0	6,0
		2173	56,0	4,5	29,0	5,8	27,0	2,3	5,2
		2166	58,0	4,0	31,0	6,5	26,8	3,0	5,3
	Intermediate orthoclases and microclines:								
13	Cherepashino (Ukraine)......	2246	61,0	5,5	33,5	8,0	27,0	4,0	7,4
14	Ilmeny (Urals), pegmatite in miaskite.....	2287	62,0	6,3	31,0	8,3	31,0	0,0	6,3
15	Ankavan (Armenian SSR), dyke of granodiorite-porphyry...................	2318	63,0	8,8	32,8	10,5	30,0	2,0	9,6
		2142	62,0	7,0	31,0	7,0	31,0	0,0	7,0
16	Annovka (Ukraine), monzonite from Novo-Ukrainian massive.................	2192	58,0	4,0	30,0	6,2	28,0	2,0	5,1
		2192	65,0	3,0	35,6	7,0	29,6	5,0	5,0
		2021	62,5	4,2	34,5	7,2	28,0	4,2	5,7
		2021	69,0	4,0	41,0	7,6	28,3	6,5	5,8
		2021	73,5	1,8	44,0	9,2	29,0	9,0	5,5
		2128	65,5	3,0	37,0	9,7	28,0	7,3	6,3
17	Kukisvumchorr II, pegmatite of Khibine massive...................	2151	62,0	5,8	33,0	6,8	29,0	2,0	6,3
		2217	63,5	4,0	35,0	8,0	28,5	4,2	6,0
		2217	63,0	4,4	32,5	6,4	30,5	2,0	5,4
18	Ortotokoi III...................	2157	66,0	5,5	34,0	6,0	32,0	1,8	5,9

TABLE I, continued

Number of spec.	LOCALITY AND ROCKS	Number of slides	−2 V°	A		B		⊥ (010) ∧ Nh	Extinction on (010)
				+ λ	+ φ	+ λ	− φ		
19	Taimir I (Taimir peninsular), syenite.....	2132	62,0	6,5	31,0	6,5	31,0	0,0	6,5
		2131	66,0	7,3	33,0	7,3	33,0	0,0	7,3
20	Buzheninov bor (Urals) pegmatite.......	2305	69,5	6,0	40,5	12,0	29,0	7,8	9,0
		2026	66,0	5,0	35,2	8,2	35,0	3,5	6,6
21	Lovozero (Kola peninsular), pegmatite....	2227	67,0	6,0	33,5	6,0	33,5	0,0	6,0
22	Tajezhnoe (Yakut ASSR), pegmatite......	2298	68,0	10,0	35,0	12,0	32,7	2,0	11,0
		2297	78,0	8,0	40,7	13,3	37,0	4,0	10,6
23	Gnivanj (Ukraine), migmatite...........	2234	65,5	7,5	32,75	7,5	32,75	0,0	7,5
		2082	75,5	6,5	37,75	6,5	37,75	0,0	6,5
		2136	66,5	4,5	39,0	9,5	27,3	6,7	7,0
		3163	74,5	7,0	37,25	7,0	37,25	0,0	7,0
24	Zhezhelev (Ukraine), precambrian garnet-cordierite granite	2055	67,0	3,8	36,3	9,0	30,3	5,0	7,6
		2135	66,5	6,0	34,2	7,8	32,2	1,8	6,9
		2249	72,0	7,5	36,0	7,5	36,0	0,0	7,5
		2301	72,5	6,3	37,8	9,0	34,2	2,5	7,6
		2247	73,0	7,5	36,5	7,5	36,5	0,0	7,5
		2248	73,0	4,0	38,5	8,5	34,7	3,5	6,2
25	Strizhevka (Ukraine), migmatite........	2165	68,0	7,5	34,0	7,5	34,0	0,0	7,5
		2245	68,0	5,0	37,0	8,5	31,0	4,0	6,7
		2058	70,0	5,8	39,2	9,5	30,5	5,0	7,6
		2058	70,0	4,0	41,7	10,0	28,0	8,0	7,0
		2244	73,0	2,0	44,5	11,0	28,0	10,2	6,5
26	Sabarov (Ukraine), garnet cordierite granite.	2036	72,0	4,0	39,3	10,0	32,5	5,0	7,0
27	Taimir II (Taimir peninsular), pegmatite..	2311	58,0	4,0	34,0	8,0	23,5	6,8	6,0
		2309	62,5	3,0	38,0	9,5	24,0	8,5	6,2
		2309	66,0	2,0	40,0	10,0	25,0	10,0	6,0
		2308	59,0	3,3	35,0	9,0	23,0	7,5	6,0
		2308	61,0	2,5	37,0	9,0	24,0	8,2	5,7
		2308	65,5	1,7	43,0	10,0	24,5	10,0	5,8
		2308	74,5	−2,0	49,0	12,0	25,0	14,5	5,0
		2310	70,0	−0,5	45,0	10,0	24,5	12,3	5,2
		2309	82,5	−4,0	57,0	12,7	25,0	18,2	4,3
28	Malaja Viska (Ukraine), porphyrytic Rapakivi granite of Korsunj massiv........	2266	70,5	8,0	36,0	10,5	35,0	2,5	9,1
29	Listvenna (the same massiv)...........	2267	74,0	9,5	37,0	9,5	37,0	0,0	9,5
30	Khlistunovka (the same massiv)........	2221	70,5	7,8	36,05	8,2	33,5	1,7	8,0
31	Shpola (the same massiv).............	2262	73,5	7,0	39,0	10,0	35,5	2,8	8,5
32	Korsunj (the same massiv)............	2264	77,5	5,0	44,7	10,0	32,7	6,5	7,5
		2255	80,0	4,0	43,5	11,0	36,0	5,5	7,5
		2256	80,5	8,3	42,5	10,2	38,0	2,0	9,3
33	Malin (Ukraine), Rapakivi granite of Korostenj massiv.	2111	80,0	7,0	42,2	12,2	37,5	4,0	9,6
34	Kapustino (Ukraine), trachytoide granite of Novo-Ukrainian massiv.............	2193	72,0	6,2	42,0	11,0	30,0	6,7	8,6
		2194	80,0	9,0	43,3	11,8	36,8	4,0	10,4

Low orthoclases and cryptotwinned microclines:

Number of spec.	LOCALITY AND ROCKS	Number of slides	−2 V°	+ λ	+ φ	+ λ	− φ	⊥ (010) ∧ Nh	Extinction on (010)
35	Voinovka (Ukraine), charnokites of Novo-Ukrainian massiv..................	2017	82,0	8,0	44,0	11,5	37,5	4,0	9,7
		2017	83,0	5,0	50,0	12,8	32,8	9,5	8,9
		2191	82,5	8,0	43,5	8,4	39,0	2,1	8,2
		2188	84,0	7,5	46,0	10,5	38,0	4,3	9,0
		2189	84,5	5,0	48,3	11,0	36,0	6,8	8,0
		2189	84,0	2,5	49,5	11,5	34,0	9,5	7,0
		2190	84,5	8,4	44,5	11,0	40,0	2,5	9,7
36	Adabash, porphyrytic charnokites of the same massiv.....................	2204	83,0	3,8	49,8	12,0	33,0	9,5	7,9
		2205	83,0	4,0	52,0	11,8	31,5	11,0	7,9
		2205	83,5	6,0	43,7	8,0	39,5	2,2	7,0
		2205	84,5	2,0	53,0	12,0	31,5	12,0	7,0
37	Kirovograd (Ukraine), trachytoid granite with garnet......................	2268	84,0	3,0	51,5	11,0	32,5	10,5	7,0
		2268	85,0	4,5	51,0	11,8	33,5	10,0	8,0
		2269	85,5	4,0	45,5	9,8	39,0	4,3	7,9
38	Khlebodarovka (near the Sea of Azov), diallage granite	2063	80,0	8,0	41,0	10,0	39,0	2,0	9,0
		2064	82,0	8,0	42,0	8,8	40,0	2,0	7,9
39	Mighija (Ukraine), migmatite...........	2275	81,0	4,0	42,0	13,0	38,5	7,0	8,5

TABLE I, continued

Number of spec.	LOCALITY AND ROCKS	Number of slides	−2 V°	A		B		⊥(010) ∧ Ng	Extinction on (010)
				+λ	+φ	+λ	−φ		
	Adularia:								
40	Astafjevo (Urals)......................	2162	36,0	5,5	18,0	5,5	18,0	0,0	5,5
		2162	40,0	5,5	20,0	5,5	20,0	0,0	5,5
		2220	62,0	4,0	34,0	6,3	28,0	4,0	5,2
41	Butughichag (Nord-East of USSR)........	2100	63,0	2,5	38,2	8,0	24,2	8,0	5,2
		2100	44,5	5,5	22,25	5,5	22,25	0,0	5,5
		2099	53,0	5,5	26,5	5,5	26,5	0,0	5,5
		2099	53,5	6,5	26,75	6,5	26,75	0,0	6,5
		2099	58,5	6,5	29,25	6,5	29,25	0,0	6,5
			62,0	6,5	31,0	6,5	31,0	0,0	6,5
	Barium feldspars:								
42 b	Inaglin (Yakut ASSR), pegmatites in nepheline syenite massiv	2092	57,0	1,7	28,5	1,7	28,5	0,0	1,7
		2130	57,5	1,2	28,75	1,2	28,75	0,0	1,2
43	Sludjanka (Lake Baikal), pegmatite	2306	73,5	1,0	36,75	1,0	36,75	0,0	1,0
	Untwinned maximum microclines:								
44	Rischorr (Kola peninsular), pegmatite of nepheline syenite.................. .	2184	83,5	−5,0	56,5	13,0	26,5	18,0	4,0
45	Zaporozhje (Ukraine), pegmatite in precambrian gneiss....................	2182	84,5	−5,0	57,2	13,0	25,7	18,2	4,0
	Cross-hatched microclines:								
46	Karelija (Karelian ASSR), ceramic pegmatite................................	2007	84,0	—	—	—	—	18,0	5,0
47	Azov, pegmatites of mariupolites........	2022	84,0	—	—	—	—	18,0	5,0

rocks and pegmatites. In this paper only few microclines with typical cross-hatch twinning and monoclinic sanidines are described. The arrangement ot specimens in the table is in the order of increasing optic axial angles.

Optical orientation determinations were made by the conoscopic method with the universal stage. A special $40 \times$ objective and special condensor were used for these measurements. The cleavage fragments of the specimens were first ground nearly perpendicular to (010) and (001) and then polished. The angles between polished plane and (010) and (001) were measured with the one-circle goniometer. Then these specimens were stuck to the slide and finally ground down to 0,1-0,05 mm. thick.

The angles between Nz, Ny, Nx, optic axes A and B (plagioclase-notation) and (010), (001) were measured and used for the construction on the Wulf net of the projection ⊥ (010) and (001). Within this plane the coordinates λ and φ were determined by the method used for determing the Becke coordinates ot the optical orientation diagram of the plagioclases. In most cases the specimens show in one grain a variation in the optic orientation and so, before measurment, the existence and distribution of this va-

riations were determined by observations of extinction in the plane ⊥ (010) and (001).

The results of the measurements are given in Table I.

Chemical analysis.—For 11 samples (numbers 3, 4, 7, 10, 20, 21, 24, 42, 43, 46, 47) standard silicate analyses and for other samples flame-photometer analyses were performed in the Central Laboratory of Chemistry of this Institute of the Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry. The results of the analyses are listed in Table 2.

X-ray Diffraction.—Single-crystal X-ray photographs (J. V. SMITH and W S. MACKENZIE technique) were made by S. V. RIKOVA. These pictures were used to detect unmixing, twinning and symmetry and to measure α^* and γ^* of triclinic phases when it was possible.

Powdered feldspars were studied, utilizing unfiltered Cu radiation with X-ray diffractometer "URS 50J". The records were used to measure the lattice spacings of the 201 reflections of if possible the angular difference between $\overline{201}$ for potassium and sodium phases of perthites, and to determine the degree of triclinicity.

TABLE II

CHEMICAL COMPOSITION AND X-RAY DATA

Spec. No	Chemical composition				X-ray Diffractometer			b-axis oscillation photographs			
	Or	Ab	An	Cs(Ba)	$\Delta 2\theta$ Cu k_α $(20\bar{1})$ Or-Ab	$d_{20\bar{1}}$	Δ	Potassium phase α^*	γ^*	Sodium phase α^*	γ^*
1	76,7	23,3	—	—	—	4,1866	0,0	—		—	
3	72,1	27,9	—	(o,n)	—	4,1788	0,0	—		—	
4	26,5	68,4	3,3	0,2	—	—	0,0	—		—	
6	—	—	—	—	1,08	—	0,0	—		—	
7	66,2	30,8	2,6	0,4	1,02	—	0,0	I		86°00	88°50'A
8	67,3	31,4	1,3	(o,oon)	1,08	—	0,0	—		—	
9	82,5	17,5	—	—	—	4,2181	0,0	—		—	
10	75,4	24,6	—	—	1,08	—	0,0 diff.	I diffuse		86°05'	88°58'A-P
11	66,2	33,8	—	—	—	—		I diffuse			A-Ps
12	88,2	11,8	abs.	(o,on)	—	4,2221	0,0	I		—	
13	—	—	—	—	1,13	—	0,0	I diffuse			A
14	80,5	19,5	0,5	0,2	1,10	—	0,0 diff.	—		—	
15	—	—	—	—	1,10	—	0,0	—		—	
16	88,2	11,8	—	—	1,13	—	0,0 diff.	I diffuse		86°21'	89°08'A-P
17	82,7	17,05	0,05	0,2	—	4,2221	0,0	I diffuse			A
18	—	—	—	—	1,10	—	0,0 diff.	I diffuse			A-Ps
20	68,7	30,6	0,5	0,2	1,14	—	0,0	I diffuse		86°11'	90°45'A-P
21	75,5	20,8	3,4	0,3	1,09	—	0,0-0,70	I		86°06'	90°39'A
22	73,2	26,2	0,4	0,2	1,14	—	0,0	—		—	
23	71,5	25,5	3,0	(o,n)	1,12	—	0,0	—		—	
24	72,4	25,5	1,3	0,8	1,10	—	0,0-0,36	I diffuse		86°36'	90°25'A
25	75,3	21,5	3,2	(o,n)	—	—		I diffuse			A
26	77,5	21,0	1,5	(o,n)	—	—	—	—		—	
27	68,9	31,0	0,1	(o,oon)	1,09	—	0,40	—		—	
28	—	—	—	—	1,10	—	0,0 diff.	I diffuse			A
30	—	—	—	—	1,14	—	0,0 diff.	—		—	
31	64,3	35,2	0,5	(o,n)	1,14	—	0,0	I diffuse		86°23'	90°40 A-P
32	64,1	34,7	1,2	—	1,12	—	0,0-0,80	I diffuse		86°31'	90°36'A-P
34	—	—	—	—	1,11	—	0,0-0,72	J		86°42'	90°30'A-P
35	65,0	34,0	1,0	(o,n)	1,10	—	0,0-0,99	J		86°20'	90°23'A
36	73,1	25,3	1,6	(o,n)	1,14	—	0,98	J		86°10'	90°31 A-P
37	66,5	30,5	3,0	(o,n)	1,09	—	0,90	J		86°20'	90°41 A
39	71,1	28,5	0,4	(o,n)	—	—		—		—	
40	—	—	—	—	—	4,2261	0,0	—		—	
41	91,2	8,8	—	—	—	—		—		—	
42	82,3	11,8	1,2	4,4	—	—	0,0	—		—	
43	70,6	17,9	1,1	10,4	1,12	—	0,0	I			A (?)
44	87,95	12,0	0,05	(o,n)	1,10	—	0,99	I		—	
45	—	—	—	—	—	—		—		—	
46	78,5	19,4	2,1	—	1,09	—	0,98	90°27¹	92°18A	—	
47	—	—	—	—	1,10	—	0,99	—		—	

A —albite twinning, P —pericline twinning, S —twinning superstructure. J —irrational twinning (=diagonal association after J. V. SMITH and W. S. MacKenzie, 1959), I —one set of reflections of potassium phase. The angles α^* and γ^* were measured by S. V. RIKOVA.

The data from these studies are shown in Table 2 and in Fig. 1.

The measurments γ^* of untwinned intermediate microcline "Taimir II" were made by S. V. RIKOVA, using Weissenberg technique.

III. OPTICAL AND STRUCTURAL RELATIONSHIPS AMONG THE POTASH FELDSPARS

The observed optical properties of "block-crystals" (twinned crytoperthites) of alkali feldspars are a complex function of submicroscopic twinning, of the degree of order and of composition of cryptoperthites and submicroscopic perthites. Extinction angles, conoscopic figures, Becke line are results of summarized influence of an aggregate of individuals. The effects of all these factors are discussed below.

Calculation of optical properties of submicroscopic twinned potash feldspars from the individual properties.—The method described in an earlier paper (MARFUNIN, 1959) was used for this calculation. The results are set down in Table 3 and plotted in Fig. 2. It follows from these data that the optic axial angle in

Fig. 1.—Diffractometer records in the region of the 131-1̄31 reflections, to show triclinicity of the investigated specimens.
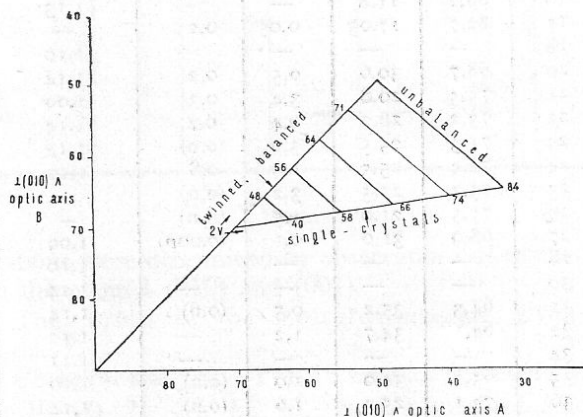
Fig. 2.—The relation between the optic axial angle and the optical orientation of untwinned and of sumicroscopically twinned potash feldspars.

a submicroscopic twinned potash feldspar is decreased very little (about 2-3°) in comparison with that of the individuals.

The results of the same calculation for albite and analbite are also given in Table 3.

Variations in optical properties caused by degree of order-disorder of Si-Al in potash feldspars.—Continuous changes of properties of crystals of the same composition are related with order-disorder phenomena. The dependence of optical properties on the order-disorder phenomena was considered in general in an earlier paper (MARFUNIN, 1956) with respect to physico-chemical analysis. The optical properties were divided into two groups: 1) more structurally

TABLE III

THE RESULTS OF OPTICAL PROPERTIES CALCULATION OF SOME SUBMICROSCOPIC TWINNED ALKALI FELDSPARS

		Ng	Np	2 V	A		B	
					Λ	φ	Λ	φ
1.	Microcline....................	1,52600	1,52000	— 84,0	— 4,0	+ 57,0	+ 12,8	— 25,5
1 a.	Twinned microcline............	1,52542	1,52050	— 81,0	+ 4,5	+ 40,5	+ 4,5	— 40,5
2.	Intermediate microcline.	1,52550	1,51950	— 74,0	0,0	+ 49,3	+ 10,3	— 24,0
2 a.	Twinned intermediate microcline..	1,52516	1,51967	— 70,5	+ 5,1	+ 35,2	+ 5,1	— 35,2
3.	Intermediate microcline.....	1,52560	1,52030	— 66,0	+ 3,0	+ 43,0	+ 9,5	— 22,5
3 a.	Twinned intermediate microcline..	1,52542	1,52046	— 63,5	+ 6,2	+ 31,7	+ 6,2	— 31,7
4.	Albite.......................	1,53920	1,52910	+ 78,7	0,0	+ 48,5	+ 39,0	— 47,2
4 a.	Twinned albite.................	1,53868	1,52911	+ 86,8	+ 20,5	+ 43,4	+ 20,5	— 43,4
5.	Analbite......................	1,53410	1,52720	— 50,0	4,0	+ 12,3	+ 20,5	— 32,0
5 a.	Twinned analbite..............	1,53360	1,52740	— 32,0	+ 9,7	+ 16,0	+ 9,7	— 16,0

sensitive properties, including optic axial angle and orientation of the indicatrix and 2) less structurally sensitive properties, including indices of refraction and birefrigence.

For the construction of the diagram of optical orientation of plagioclases (MARFUNIN, 1958, 1960) those extreme values were used, which were observed in low-temperature and in heated specimens. The values are only marking ones for the disorder and order states.

The optical properties of potash-soda feldspar have the same structural significance as the X-ray constants which describe lattice geometry.

Optic axial angle in potash-soda feldspars change little with a change of the composition of cryptoperthites (as will be indicated below) and is virtually independent of submicroscopic twinning.

The optic axial angle changes from — 84° to 0° and then to — 60° ∥ (010), i.e. through 144°. This has been observed in natural potash feldspars and takes
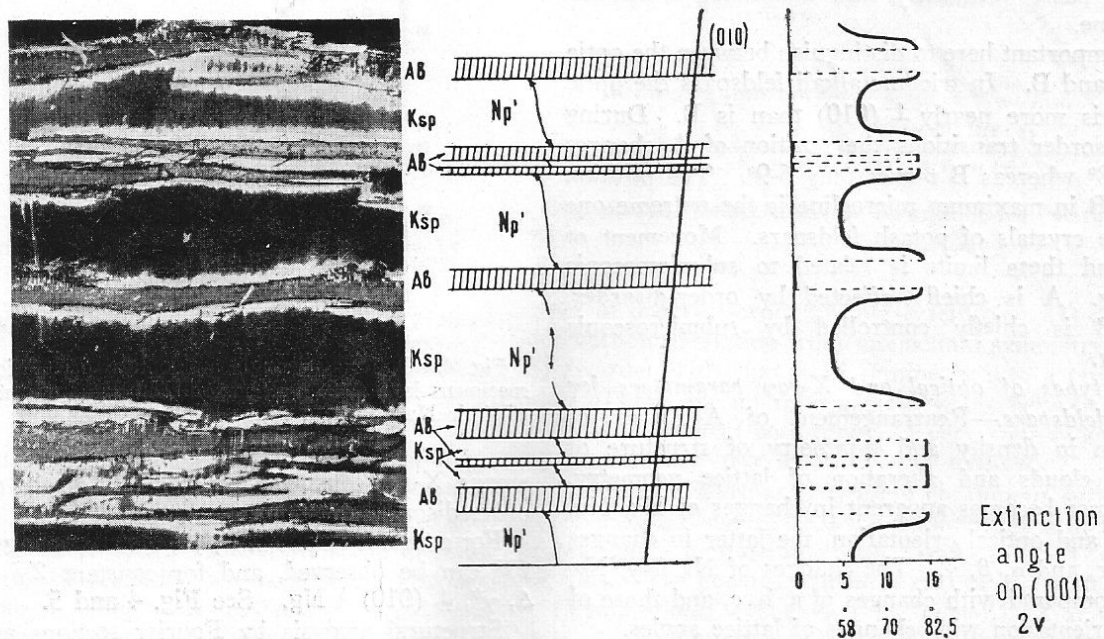

Fig. 3.—Microphotograph of a thin section ∥ to (001) of «Taimir II» showing the distribution of the change from intermediate to maximum microcline and associated changes in optical properties.

place by heating. This change can be related only to variations of the degree of order-disorder.

Optical orientation has a great significance in the study of transformations in solids which are accompanied by change of the symmetry. Transitions from disorder in the high-temperature form of potash feldspar to order in the low-temperature form are accompanied by the change from monoclinic optical orientation to triclinic. When there is an approach to an ideal perfectly ordered arrangement the orientation of indicatrix is that of microcline with maximum triclinicity.

However, optical orientation depends also on submicroscopic twinning. Direct observations were made by the study of specimens "Voinovka", "Adabash", "Kirovograd" (Table 1 and 2, NN 35-37). (They have nearly the maximum degree of triclinicity ($\Delta \approx 0.9$) and optic axial angle — $2V = 82\text{-}85°$ and show twinning on the b-axis oscillation photograph, but due to very fine twinning have an integrated optical orientation, nearly monoclinic or intermediate between monoclinic and maximum microcline. The pure untwinned potash feldspar of the unique specimen "Taimir II" (N 27 in Table 1 and 2) shows the states intermediate between sanidine and maximum microcline. It consists (Fig. 3) of large (1-5 mm.) veins of potash feldspar which alternate with albite veins (0.2 — 1.0 mm). In the middle of the veins, the potash feldspar is intermediate microcline with triclinicity intermediate between sanidine and microcline and with intermediate positions for all optic directions. Near the Ab-perthite veins the potash feldspar passes gradually into untwinned maximum microcline.

It is important here to distinguish between the optic axes A and B. In triclinic alkali feldspars the optic axis A is more nearly $\perp$ (010) than is B. During order-disorder transitions the position of A changes about 38° whereas B moves only 6-9°. The position of axis B in maximum microcline is the extreme one of single crystals of potash feldspars. Movement of B beyond these limits is related to submicroscopic twinning. A is chiefly affected by order-disorder, while B is chiefly controlled by submicroscopic twinning.

Two types of optical and X-ray parameters for potash feldspars.—Rearrangement of Al-Si causes alteration in density and symmetry of structure of electron clouds and alteration of lattice geometry. The former becomes apparent in changes of Nz, Ny, Nx, 2V and optical orientation, the latter in changes of a, b, c, and α, β, γ. The changes of Nz, Ny, Nx can be compared with changes of a, b, c, and those of optical orientation with changes of lattice angles.

It is to be noted that there is no X-ray parameter which is sensitive to small changes in a, b, c, in the way as 2V is sensitive to small changes in Nz, Ny, Nx.

Due to these consideration the parameters of potash feldspars can been divided in two groups:

1) optical orientation; degree of triclinicity; lattice angles;

2) optic axial angle.

The parameters of the first group depend on the degree of order-disorder and on submicroscopic twinning. Optic axial angle which is the only parameter of the second group and which has no analogue
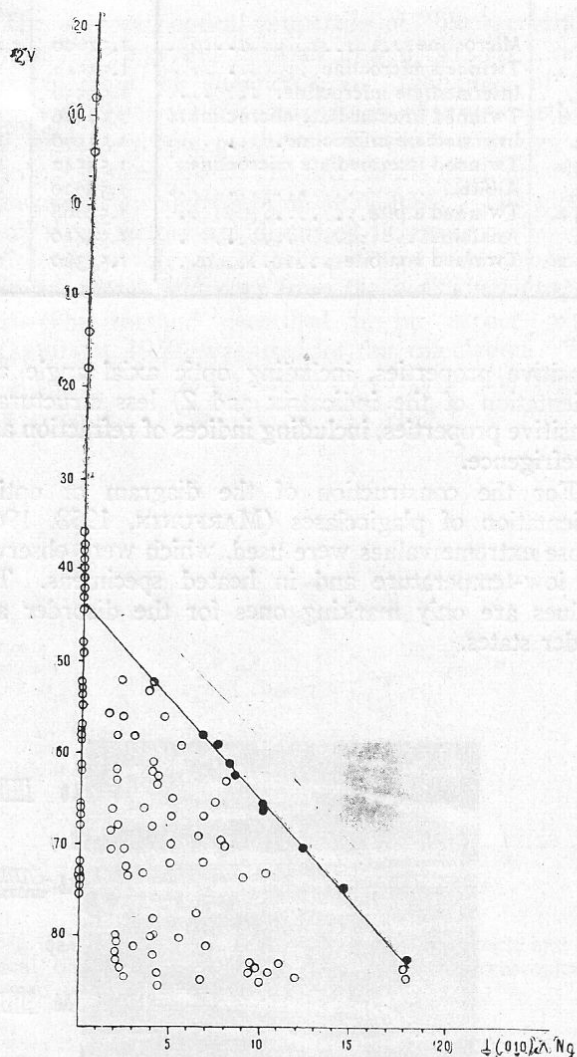
Fig. 4.—Optic axial angle and optical orientation for the specimens investigated. The solid circles represent specimen «Taimir II».

among X-ray constants depends only on the degree of order-disorder.

For constant values of Δ, γ^*, $\perp$ (010) $\wedge$ Ng different 2V can be observed, and for constant 2V different Δ, γ^*, $\perp$ (010) $\wedge$ Ng. See Fig. 4 and 5.

Structural analysis by Fourier sections and other methods cannot be used for the estimation of degree of order-disorder in potash feldspars, because in the structural analysis a lattice geometry is involved which

depends also on sub- X-ray twinning. The comparison of 2V and γ* in specimens "U" (SPENCER, 1937; BAILEY and TAYLOR, 1955) and "Taimir II" (Fig. 5) shows that the properties of "U" are not only due to degree of order-disorder. From the distances

are all monoclinic. In this region the "unstable feldspars" of HAFNER and LAVES (1957) were not observed. Potash feldspars with optic axial angles of more than ~ 44° show variable symmetry for constant 2V.

This relation makes it possible to describe the varieties of potash feldspars as follows. There are two

Fig. 5.—Optic axial angle and triclinicity Δ, γ*; small circles — Δ (X-ray Diffractometer), large circles — γ* (Weissenberg technique), solid circles — «Taimir II» and «u» (SPENCER, 1937; BAILEY and TAYLOR, 1955).

Fig. 6.—The interrelations of variants of the potash feldspars.

cation — 0 and from lattice angles α^* and γ^* the degree of triclinicity and degree of order-disorder must be near to 0.32 (BARTH, 1959). However, from Fig. 5 the degree of order-disorder must be near to 0.8 and degree of triclinity which depends also on submicroscopic twinning near to 0.32.

Interpretation of potash feldspars.—Fig. 5 and 6 are diagrams whose coordinate axes are the two groups of constants mentioned above. They show that the potash feldspars with small optic axial angles

types of order-disorder in potash feldspars: 1) disorder without deviation from monoclinic symmetry and 2) disorder with change of symmetry into a triclinic one. There are all intermediate states between disorder ond order of both types. Every state of substitution disorder may be sub-X-ray twinned.

The potash feldspars represent continuous series of order-disorder states. All the triclinic forms of these states have innumerable sub-X-ray twinned polymorphs. The general scheme is set out in Fig. 6.

Crytoperthites.—The data of Table 1, 2 and the data of MACKENZIE and SMITH (1959) show that the K-rich feldspars with optic axial angles more than 40-45° are perthites.

The composition of the separate phases of perthites

was determined by the distance ($\Delta 2\theta$) between the reflections $20\bar{1}$ of potash and soda phases. This calculated distance is 1.03° when both phases represent pure disorder components and it is 1.125° when the perthite consists of disordered $KAlSi_3O_8$ and ordered $NaAlSi_3O_8$ (from the data of DONNAY and DONNAY 1957; GOODYEAR and DUFFIN, 1954). The effects of other components (Ca, Ba) and of order-disorder changes decreases this distance. The investigated perthites show a range of $\Delta 2\theta$ ($20\bar{1}$) from 1,08 to 1.14° (in one case it is 1.02°).

If the strain produced by the unmixing (LAVES, 1952) does not exclude the possibility of using the $20\bar{1}$ method on cryptoperthites, the measured values probably show that the perthites consist of nearly pure components and that the sodium phase is more ordered than the potash phase. The angles α^* and γ^* indicate the same. The sodium phase is always twinned so that their integrated optical symmetry must be pseudo-monoclinic when the twinning is balanced. The integrated properties of perthites consisting of nearly pure components are obtained by addition as the properties are those of a mechanical mixture.

The tentative estimation of the composition of cryptoperthites can be made by the diagram Fig. 7.
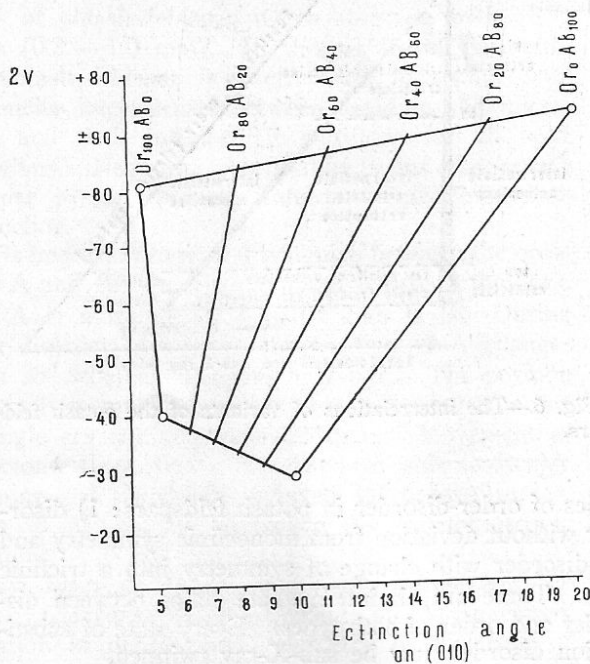

Fig. 7.—Diagram for the determination of Or: Ab relations in cryptoperthites.

IV. THE DIAGRAM OF THE OPTICAL ORIENTATION OF POTASH-SODA FELDSPARS

On the basis of the measurements (Table 1) and of the structural interpretation of potash-soda feldspars the diagram Fig. 8 was constructed. The analysis of the position of all optical directions permits conclusions to be made about the structural features and chemical composition of alkali feldspars. This diagram indicates the restriction of possible relationships between the various optical constants and also shows the limits in the ranges of these constants.

V. SOME PETROLOGICAL CONCLUSIONS

Many petrological papers have described the alteration of orthoclase into microcline going hand-in-hand with variation of triclinicity. This may be due to two different phenomena: *a)* enlargement of twinning observed especially near the inclusions of quartz, plagioclase and other minerals, which represent here a kind of counterfort, *b)* transition from less to more ordered states.

The variations of optical orientation which accompany these two types of transformation are different: in the former case only the orientation of the indicatrix changes with near constancy of the optic axial angle and both optic axes A and B move equally; in the latter case 2V also changes and A moves more quickly than B.

Therefore there is no fixed point of a transition orthoclase $\rightleftarrows$ microcline. Thus, the division of granites into orthoclase granites and microcline granites must be more precisely defined. Quite different feldspars have been described as orthoclase: the crypto-cross-hatched microcline of charnokites (specimens 35, 36), intermediate-low orthoclase of Rapakivi granites (specimens 28-33), intermediate orthoclase of garnet-cordierite granites and migmatites (specimens 23-26), high orthoclase of tertiary granites (specimen 7).

Adularia and ferriferous orthoclase are not new structural variants. They represent only morphological or chemical variants of sanidines, high or intermediate orthoclases and other structural variants. The distribution of structural variants in magmatic and metamorphic rocks is of regional nature. For instance in Ukrainian Pre-Cambrian there are only four types of potash-soda feldspars.

Magmatic rocks and related pegmatites, migmatites, porphyroblasts in xenolithes, druses contain the same variety of potash-soda feldspar.

Comparison of the effect of unmixing, order and twinning which coexist in many specimens, shows a succession in formation of these phenomena. All potash-soda feldspars with small degrees of order-disorder are unmixed and, also, usually twinned, the Na-phase being submicroscopically, the K-phase sub-X-ray twinned. Polysynthetic twinning occurs after crystallization and is controlled by unmixing. When the temperature decreases the minimum value of the
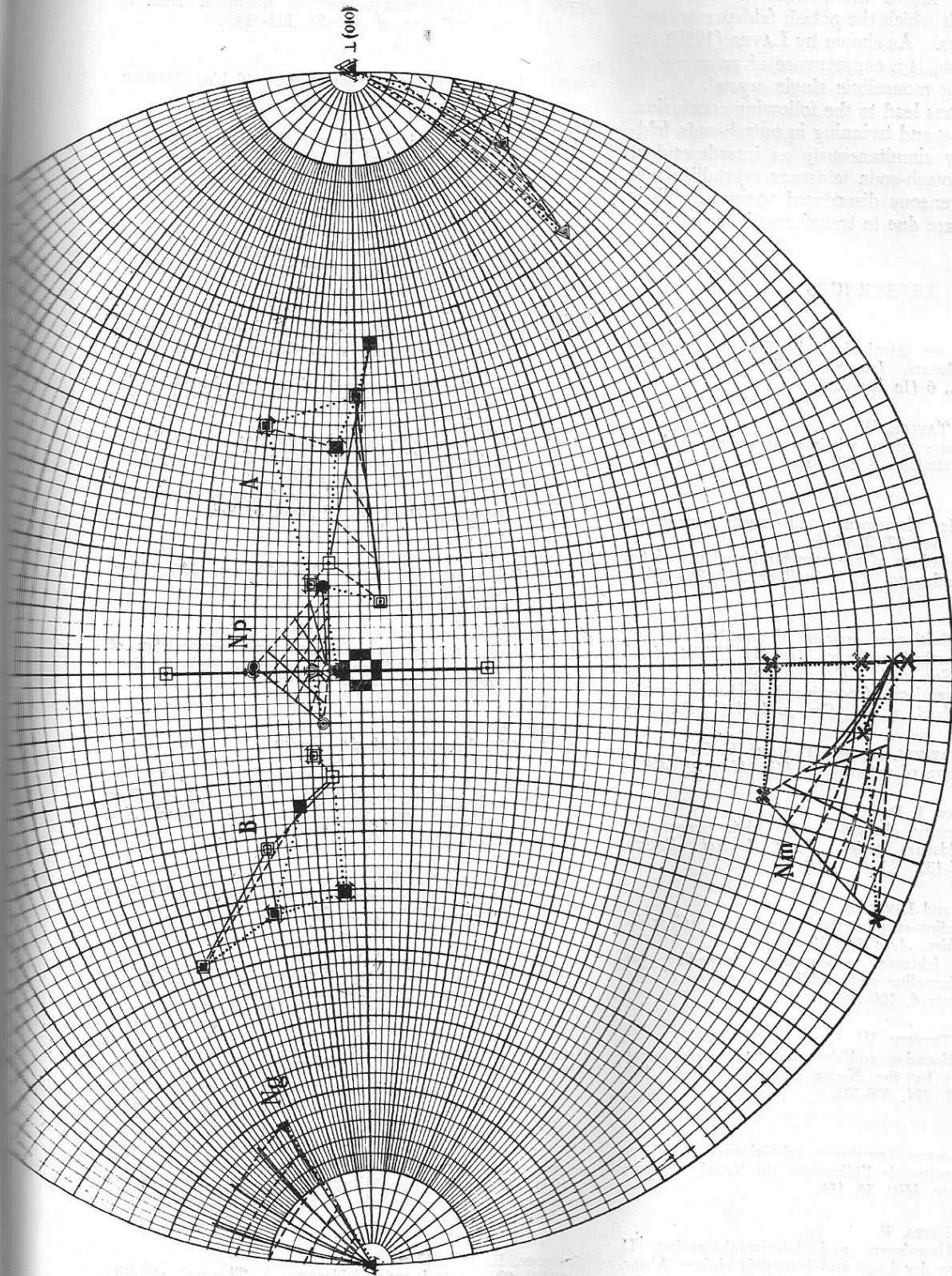
Fig. 8.—Diagram of optical orientation potash-soda feldspars.

○ Disordered K-fsp (sanidine)
● Ordered K-fsp (microcline)
◉ Disordered Na-fsp (analbite)
◉ Ordered Na-fsp (albite)

microcline ⎫
analbite ⎬ Submicroscopilly twinned.
albite   ⎭

optic axial angle shows the maximum degree of order-disorder with which the potash feldspar crystallized from the melts. As shown by LAVES (1950) the cross-hatch twinning is a consequence of an inversion from a pre-existing monoclinic single crystal.

These observations lead to the following conclusion. Unmixing, ordering and twinning in potash-soda feldspars occur nearly simultaneously as interdependent processes. The potash-soda feldspars crystallize metastably as homogeneous disordered variants. Their observed features are due to transformations in solids.

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Alkali feldspars from some intrusive porphyries of Southwestern United States

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ABSTRACT

Powder X-ray diffraction analysis of the ($\bar{2}01$) reflections of many perthitic alkali feldspars at room temperature, 750°C., and 1050°C. shows considerable differences which appear to be a function of the relative temperature-structural states of the feldspars. Sanidines remix more rapidly and completely than microclines, whereas orthoclases show all intermediate stages. Variation in rate and completeness of remixing appears to be independent of bulk composition, although the ultimate cause may well be affected by impurity elements and/or lattice defects.

The average bulk composition of the feldspars studied (225) is about $Or_{69}(Ab + An)_{31}$ weight percent, and the compositional range for any porphyry is 20 to 40 + weight percent. Perthitic remixing is accomplished faster and more completely in feldspar specimens from those parts of an igneous sequence which are more porphyritic (Globe-Miami, Arizona; Rabb Canyon, and Hillsboro, New Mexico), more pegmatitic (Rabb Canyon), more eruptive (La Sal Mountains, Utah), and/or more orebearing (Ajo, and Globe-Miami, Arizona; Questa, New Mexico). Thus the perthitic alkali feldspars showing the relatively highest temperature-structural states appear to be found in those parts of an igneous sequence which show the most hydrothermal features.

Such a method of comparing alkali feldspars from an intrusive appears to have value for igneous petrogenesis, as well as ore distribution. The results provide additional evidence of a genetic association between igneous crystallization and ore deposition.

INTRODUCTION

Many studies of mineral variation within homogeneous rock units have been and are being made in order to obtain a better understanding of the conditions of origin of the rock mass. For hypabyssal igneous rocks one may likewise expect rock properties to vary systematically throughout the rock mass according to the conditions of origin, unless all parts of the intrusive have approached identical equilibrium states to the same degree. The present paper, which has been assisted by a research grant from the National Science Foundation, is an attempt to apply some of the newer data on alkali feldspars (Laves, 1950, 1952; Goldsmith and Laves, 1954 a, b; Mac-Kenzie and Smith, 1955, 1956; Tuttle and Bowen, 1958) and newer X-ray techniques (Birks and Friedman, 1947; Weiss and Rowland, 1956; Bassett and Lapham, 1957) to a study of some Tertiary porphyries of the United States.

Porphyries common throughout the western mountains of both North and South America show a full range in composition from andesite to granite and appear to be hypabyssal (shallow to intermediate depth). Many of the more granitic varieties, of which quartz monzonite may be most common, are about middle Tertiary in age and contain numerous alkali feldspars. Such alkali feldspars are, for the most part, perthitic on an X-ray or microscopic scale, and exhibit the optical properties of sanidine or orthoclase.

In an igneous rock such as a porphyry, the first alkali feldspars would be a homogeneous sanidine which upon cooling should separate into two phases, forming a perthite (Laves, 1952). This unmixing reaction, which might be written, Homogeneous feldspar $\longleftrightarrow$ cryptoperthite $\longleftrightarrow$ macroperthite, is readily reversible under laboratory conditions (Tuttle and Bowen, 1958), although no optically-visible exsolution has been produced. Under simple cooling conditions of an igneous mass, without dynamic metamorphism, the above reaction should proceed to the right, but in most Tertiary porphyries is far from complete. The basic idea of this study was to take a natural alkali feldspar, subject it to various heat-treatments, and compare the extent to which these heat-treatments displaced the unmixing reaction (above) toward the homogeneous feldspar state. The more readily and completely this remixing occurred for any set of laboratory conditions, presumably, the closer the natural feldspar was to its original high-temperature state. One should remember that a high-temperature form may arise through low-temperature inequilibrium crystallization.

However, numerous data are available suggesting that the foregoing hypothesis is subject to considerable limitation and has value primarily in providing geologic-petrographic comparisons. First, Goldsmith and Laves (1954 b) have shown that numerous crystals of similar unmixing status are composed of a range of monoclinic to triclinic states. Such variations occur even within single morphological units.

In using alkali feldspars as a petrographic guide, therefore, it is desirable to study as many morphological units per hand specimen as possible. This in turn almost precludes using single-crystal X-ray diffraction techniques because of the tremendous difficulty involved in adequately summarizing the structural features of all the alkali feldspars in a hand specimen. Second, recent studies of crystal-growth and phase relations demonstrate that even many of the most important crystallographic and solid-state system properties are dependent on impurity elements and lattice defects. Differing concentrations of trace elements such as Li, Rb, and Sr may reflect such differences in pressure-temperature-crystallization rate that variation in perthitic unmixing should not be surprising. These limitations exist in most crystallographic studies of materials from widely separated geological environments.

METHOD OF MEASUREMENT

In order to compare alkali feldspars from an igneous rock or several igneous rocks, many of which may be rather fine-grained, it is necessary to obtain adequately precise compositional and structural data from numerous small-size samples. Bulk compositions of the alkali feldspars are based on (1) spectrographic analysis of Na, K, Ca, Ba, etc. ($\pm$ 5-10 % of the element present), and (2) position of the ($\overline{2}01$) reflection of heated alkali feldspars (heated more than 48 hours at 1050°C). Each group of spectrographically-analyzed samples included four repeatedly-analyzed feldspar standards. The maximum measured range of the analyses of the feldspar standard compositions was 5.6 wt. % orthoclase (see KUELLMER, 1960 a) and for this reason the spectrographically-analyzed compositions are believed accurate to $\pm$ 5 wt. % orthoclase. Measurement of the ($\overline{2}01$) reflection of heated alkali feldspars, according to BOWEN and TUTTLE, provides only a measure of the orthoclase percent of the total Or + Ab + An. Although the heat-treatment was not sufficient to sanidinize the alkali feldspars, the orthoclase weight percent of the X-ray determined compositions is believed accurate to within a minus 7 % and plus 3 wt. % (see ORVILLE, 1958; KUELLMER, 1960 b).

In using the compositional determinations the alkali feldspars are regarded as a two-component mixture, namely an orthoclase-rich phase and an albitic plagioclase, ignoring the calcic plagioclase component. In an analogous manner plagioclase optical properties are commonly used as a measure of the bulk composition, ignoring the potassium component. An additional justification for this is that the material here studied, with the exception of specimens from the La Sal Mountains, Utah, had morphological and optical properties of a potash-rich feldspar, namely sanidine, or-

thoclase, or microcline. The calcic plagioclase component is most likely to be important in those alkali feldspars which are sodium-rich. Furthermore every attempt was made to correlate the X-ray properties herein described with the calcium content of the alkali feldspar, where known, with little success.

The 2θ position of the ($\overline{2}01$) reflection from both phases of the perthite, or one phase of the heated homogeneous-appearing perthite was measured on a Norelco Phillips X-ray goniometer using an internal standard, and are believed accurate to within 0.02°2θ.

X-ray measurements were made of the variation of the ($\overline{2}01$) spacings with time and temperature of heating by means of a furnace built onto a Phillips X-ray goniometer diffractometer. This furnace was a modification of one built by G. L. DAVIS of the Geophysical Laboratory who generously furnished the author with complete plans and photographs of his apparatus. This furnace was calibrated by (1) melting various compounds and noting the temperature at which characteristic X-ray reflections disappeared, (2) measuring the thermal expansion of lattice spacings of extremely pure Pt and Ag powders, and by (3) auxiliary thermocouples placed at various points on the upper surface of the powdered sample. The recorded temperature is believed accurate to $\pm$ 20°C, and the ($\overline{2}01$) spacings at higher temperatures accurate to $\pm$ 0.05°2θ.

Feldspar powders, prepared, mounted and heated in exactly the same way, were X-rayed during heat-treatment by means of this furnace. Samples were heated from room temperature to 750°C in a uniform manner, and maintained at this temperature in general for periods of more than 10 hours, and as much as 30 hours, during which time the position of the ($\overline{2}01$) reflection was recorded. During this heat-treatment the ($\overline{2}01$) spacing of the potassium-rich phase of a perthitic alkali feldspar increases as a consequence of the temperature-increase, or if any remixing of the perthite phases occurs, decreases (or increases less than the normal amount). The reason for the decrease in the ($\overline{2}01$) spacing during heat-treatment is that the potassium-rich phase of the perthitic alkali feldspar accepts more sodium (see BOWEN and TUTTLE, 1950). For a homogeneous sanidine the ($\overline{2}01$) spacing is proportional to the sodium-potassium composition (see TUTTLE and BOWEN, 1958). The more readily and completely the ($\overline{2}01$) spacing of a perthitic feldspar, during and after heat-treatment, corresponds to that expected from the bulk composition, the less the natural perthitic feldspar has unmixed from its original homogeneous high-temperature state.

COMPOSITIONAL VARIATION

Table I presents the bulk composition of a large number of perthitic alkali feldspars from intrusive

Table 1

APPROXIMATE BULK COMPOSITION OF THE EXAMINED PERTHITIC ALKALI FELDSPARS

Locality in U. S. A.	Rock Unit	No. of Samples in Each Compositional Range [a]								
		21-30	31-40	41-50	51-60	61-70	71-80	81-90	91-100	Total No.
Mt. Pennell Utah [b]	Qz. Monz. Por.				4	1				5
	Rhyolite Tuff			2		7	3			12
Grant Co., New Mex.	Sanidine Por.				2	14	4			20
	Sanidine Pegmatite					1				1
Idaho [c]	Tert. Por.			1	2	2				5
Hillsboro, New Mex.	Qz. Monz. Por.			1	18	10	2			31
Questa, New Mex. [d]	Soda Granite		1		1	3	6	3	2	16
La Sal Mts., Utah [b]	Diorite Por.			1	1					2
	Monz. Por.		2				1			3
	Syenite			1			1			2
	Feld. Sy. & Gr.	1	2		1			1		5
California-Idaho-Washington	Nevadan Intrus. [e]				2		6	1		9
Miami, Arizona	Lost Gulch Qz. Monz.					3	11	14	4	32
	Gr. Por.					3	7	3		13
	Schultze Granite					1	6			15
Ajo, Arizona	Cornelia Qz. Monz.	1				3	9	1		14
Twin Buttes Quad. Ariz. [f]	Porphyry					1	7	1		9
	Tertiary						12	2		14
	Mig.					2	3			5
	pre Cambr.					2	4			6
	Vein Peg.					1	2	1		4

[a]. Composition range given in Orthoclase weight percent of the total Or + Ab + An content.
[b]. Samples from C. B. Hunt.
[c]. Samples from W. B. Hamilton.
[d]. Samples from J. H. Schilling.
[e]. Samples from W. B. Hamilton, C. A. Hopson, and A. C. Waters.
[f]. Samples collected with J. Cooper. Rock unit names are field terms, representing different textures.

rocks of the western United States, expressed in terms of Or weight percent of the total Or + Ab (+ An) content. The compositions summarized in Table I are believed accurate to within about 10 weight percent. This includes both spectrographically and X-ray determined compositions.

The table demonstrates that even a small homogeneous hypabyssal porphyry may exhibit a considerable range of alkali feldspar bulk composition. The average bulk composition of all alkali feldspars in Table I is 69 weight percent orthoclase. It may be significant that all the Arizona samples (Ajo, Miami, and Twin Buttes) are richer in orthoclase content than the New Mexico samples (Questa, Hillsboro, and Grant County). All of the sample groups, with the exception of the La Sal specimens and one Ajo specimen, contain more orthoclase than albite (and anorthite) and do not extend across the compositions of the minimum-temperature trough of the system-$NaAlSi_3O_8$-$KAlSi_3O_8$ (TUTTLE and BOWEN, 1958).

THERMAL EXPANSION OF ($\overline{2}$01) SPACINGS OF HOMOGENEOUS ALKALI FELDSPARS

In order to compare remixing rates of the perthitic alkali feldspars during heat-treatment, information concerning the expansion properties of homogeneous alkali feldspar phases is necessary. Such data are presented in Figure 1. Note that the figure shows the measured 2θ positions (for CuKα radiation) plotted against the temperature, instead of the actual lattice spacing. All the feldspars here depicted show about the same decrease in 2θ, namely 0.20 degrees, between room temperature and 740°C. For this reason the ($\overline{2}$01) thermal expansion is believed to be the same magnitude for all homogeneous alkali feldspars regardless of temperature state or composition.

Both the high and low albite (Fig. 1) samples are from the same material, one part of which was heat-treated (KUELLMER, 1959, p. 656) and the other not. The composition of this albite from a pegmatite near Ribera, New Mexico is $Or_{0.3}Ab_{94}An_5$ ($\pm$ 5) wt. % (KUELLMER, 1960a). The difference between the high and low-form curves may well be due to a slight compositional difference in the high-form, as a result of the heat-treatment which would remix all Na, Ca, and K to a more homogeneous phase.

The homogeneous moonstone (Fig. 1) refers to a moonstone sanidine specimen from a high-temperature pegmatite in Rabb Canyon, Grant County, New Mexico which was heated to 900°C for several days to remix the perthitic phases. A bulk composition of $Or_{63}Ab_{34}An_3$ ($\pm$ 5) wt. %, was determined by spectrographic analysis (see KUELLMER, 1960a). A part of the moonstone specimen was quenched; i.e. cooled to room temperature in less than one minute;

whereas a second part was annealed, i.e. cooled to less than 100°C in about 10 hours. Samples from both quenched and annealed parts of this moonstone specimen show no pronounced differences in thermal behavior.

Linear thermal expansion of three microcline specimens from pegmatites in northern New Mexico is shown by the squares, triangles, and black dots adjacent to the word "Microclines" in Figure 1. The specimen indicated by the black dot has an approximate composition of $Or_{78}Ab_{22}$ ($\pm$ 5) wt. %, based on spectrographic analysis, and therefore may contain some albite; whereas the composition of the other specimens is unknown.

The sanidine expansion (Fig. 1) is based on a synthetic sanidine ($KAlSi_3O_8$), crystallized at 800°C and 1000 bars water pressure for a period of six days, and generously loaned to the author by PHILIP M. ORVILLE of the Geophysical Laboratory. The difference between the microcline and sanidine variations is probably due to the sodium content of the natural microclines.

For comparision (Fig. 1), the thermal expansion of the (10$\overline{1}$0) spacing of part of a large oscillator-grade quartz crystal is shown. The quartz determinations were made because many of the natural perthite feldspars were so poikilitically intergrown with quartz that complete quartz removal during sample preparation appeared impossible. Each set of symbols (circles, squares, black dots, etc.) in Figure 1 for quartz refers to replicate determinations on the same powdered quartz, and thus furnishes some idea of the reproducibility of the measurements. The measurements in the vicinity of the low-high quartz transition are less accurate than the remaining points, for the reflections were changing more rapidly than they could be recorded by the Geiger counter. The change in 2θ from room temperature to 750°C for the quartz here studied is about 0.30°, and that illustrated by BASSETT and LAPHAM (1957) for a similar temperature range is about 0.36°.

COMPARATIVE REMIXING OF PERTHITIC FELDSPARS

Sanidine and Microcline Perthites.

Figure 2 shows the variation of the ($\overline{2}$01) reflections for the potash-rich phase of various sanidine and microcline perthites as a function of the time of heat-treatment at 750°C. The vertical scale for this figure and all similar subsequent figures is the 2θ value (for CuKα radiation) of the potash-rich ($\overline{2}$01) reflection. The horizontal scale is the duration of the heating cycle at 750°C in hours. During the first hour and a half, the sample temperature was being raised from room temperature to 750°C. This is indicated
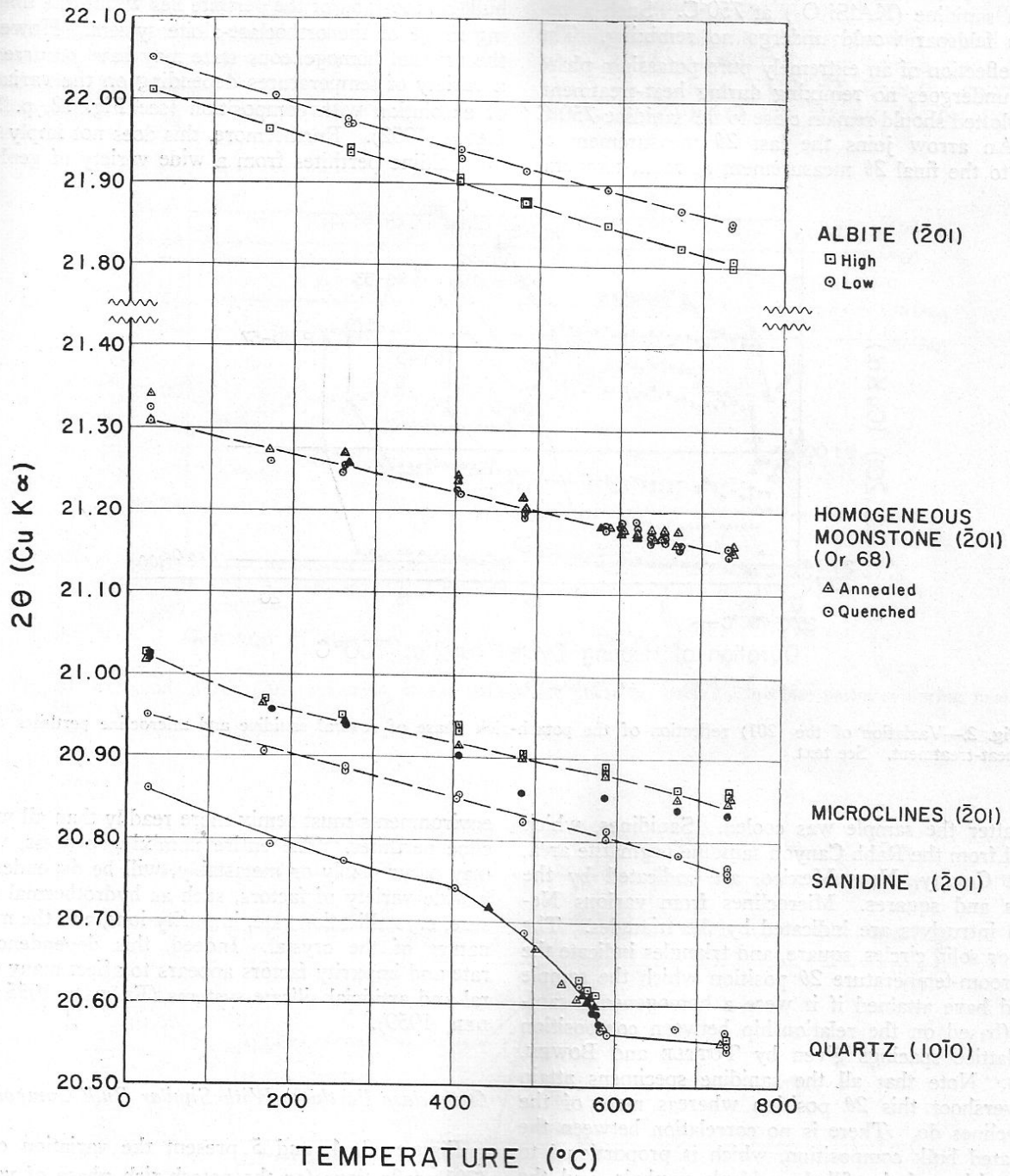
Fig. 1.—Thermal expansion of the ($\bar{2}$01) reflections of some homogeneous alkali feldspars, and for comparison the thermal variation of a (10$\bar{1}$0) quartz reflection.

along the abscissa and is reflected in the continual decrease in 2θ during the time from 0 to 1½ hours. The horizontal line labeled Exp Or_{100}, which is added as a reference, indicates the 2θ position for a pure potassium sanidine ($KAlSi_3O_8$) at 750°C. Such a potassium feldspar would undergo no remixing. The ($\bar{2}01$) reflection of an extremely pure potassium phase which undergoes no remixing during heat-treatment, when plotted should remain close to the sanidine-750°C line. An arrow joins the last 2θ measurement at 750°C to the final 2θ measurement at room temperature after the sample was cooled.

From this, it is concluded that, in a general way, the more readily and completely remixing takes place, the closer the natural perthite is to its original homogeneous or high temperature-structural state if the bulk composition of the perthite lies within the unmixing range of the orthoclase-albite system. However, the original homogeneous state may have occurred at a variety of temperatures depending on the variation of exsolution with composition (see Fig. 12, p. 561, LAVES, 1952). Furthermore, this does not imply that all sanidine perthites from a wide variety of geologic
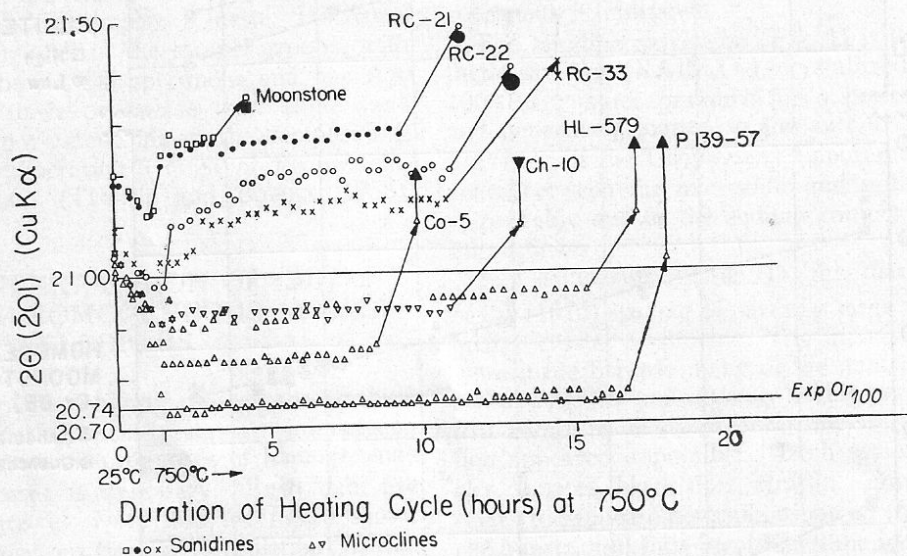

Fig. 2.—Variation of the ($\bar{2}01$) reflection of the potash-rich phase of several sanidine and microcline perthites during heat-treatment. See text.

ture after the sample was cooled. Sanidines, which are all from the Rabb Canyon sanidine pegmatite area, Grant County, New Mexico, are indicated by the circles and squares. Microclines from various Nevadan intrusives are indicated by the triangles. The filled or solid circles, square, and triangles indicate the final room-temperature 2θ position which the sample should have attained if it were a homogeneous sanidine (based on the relationship between composition and lattice spacings given by TUTTLE and BOWEN, 1958). Note that all the sanidine specimens attain or overshoot this 2θ position whereas none of the microclines do. There is no correlation between the estimated bulk composition, which is proportional to the position of the filled or black symbols, and the nature or extent of remixing. Even identical bulk compositions for sanidines (RC-22 and RC-33) and microclines (HL579 and P139-57) show considerable variation in the behavior of the ($\bar{2}01$) reflection with uniform heat-treatment.

All the sanidine perthites in Figure 2 remix more completely and readily than the microcline perthites.

environments must remix more readily than all microcline perthites. The entire unmixing process, which may occur stably or metastably, will be dependent on a wide variety of factors, such as hydrothermal pressure, crystallization rate, impurity ions, and the mosiac nature of the crystal. Indeed, this dependence on rate and impurity factors appears to affect many natural and artificial silicate systems (FLÖRKE, 1955; YODER, 1959).

Orthoclase Perthites With Similar Bulk Composition.

Figures 3, 4, and 5 present the variation of the ($\bar{2}01$) reflections for the potash-rich phase of various orthoclase perthites as a function of the time of heat-treatment at 750°C. The composition of all these orthoclase perthites, based on spectrographic analysis, falls within the range Or_{58} to Or_{65}. All these perthite specimens are from Tertiary (or late Cretaceous) intrusives and the numbering scheme is identical to that previously used (see KUELLMER, 1960 a). Fi-

gures 3 to 5 are similar to Figure 2, with the addition of four horizontal reference lines indicating the expected 2θ position of homogeneous sanidines with the bulk compositions ($Or_{58}Ab_{62}$) and ($Or_{65}Ab_{35}$), at room temperature (indicated by "Or_{58}" and "Or_{65}") and at 750°C (indicated by "Exp. Or_{58}" and "Exp. Or_{65}"). The 2θ position of the potash-rich ($\bar{2}01$) reflection within this field gives some idea of the composition and extent of remixing.

Comparison of Figures 3 to 5 with Figure 2 shows that the twelve orthoclase perthite specimens, both in their 2θ positions at 750°C and in their remixing pattern, show all intermediate states between sanidine and microcline. If no remixing occurred, and if the potash-rich phase were nearly pure $KAlSi_3O_8$ the reflection would occur at $20.74°2\theta$. If complete remixing occurred the ($\bar{2}01$) reflection should lie between 21.14 and $21.21°2\theta$ for compositions Or_{58} to Or_{65}. A specimen (H126-52) from the quartz monzonite porphyry of the HENRY MOUNTAINS, Utah
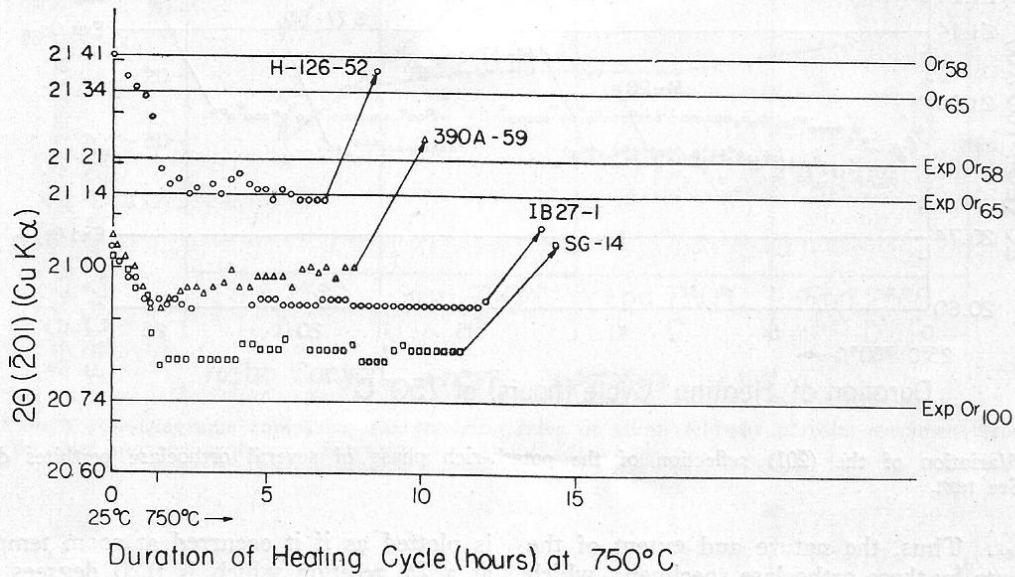

Fig. 3.—Variation of the ($\bar{2}01$) reflection of the potash-rich phase of several orthoclase perthites during heat-treatment. See text.
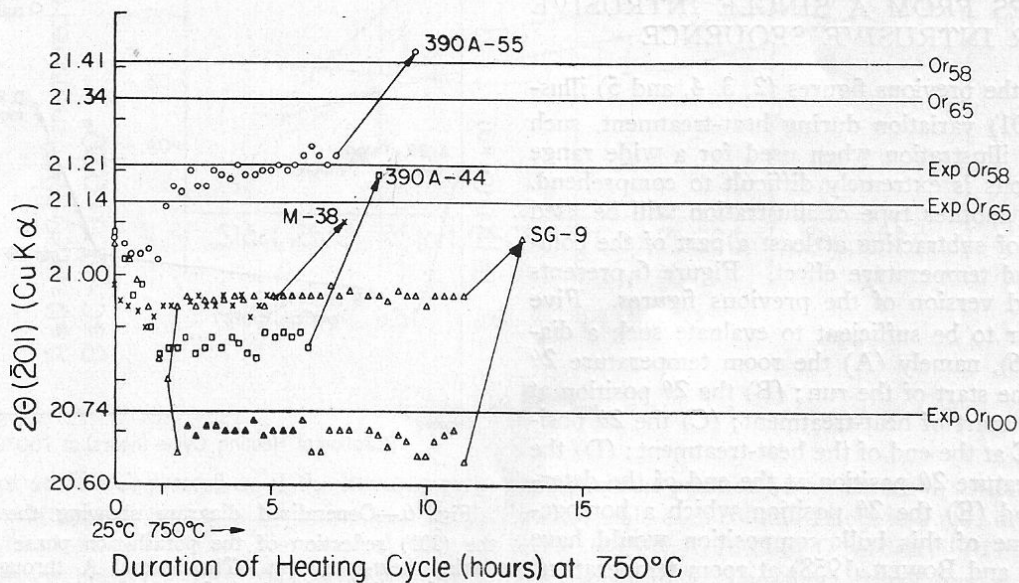

Fig. 4.—Variation of the ($\bar{2}01$) reflection of the potash-rich phase of several orthoclase perthites during heat-treatmen. See text.

shows (Fig. 3) a potash-rich $(\overline{2}01)$ reflection indicating even less unmixing than the sanidines (Fig. 2). A specimen (SG-9) from the Schultze granite near Miami, Arizona during heat-treatment shows (Fig. 4) two potash-rich $(\overline{2}01)$ reflections, one at about pure $KAlSi_3O_8$, and a second at a position corresponding

should decrease in 2θ about 0.20° $(CuK\alpha)$ for a temperature increase from 25°C to 750°C. If one then adds the value 0.20 to all the 2θ positions at 750°C (points B and C above), all the $(\overline{2}01)$ reflection positions may be compared on a room-temperature basis. The shift in 2θ as a result of heat-treatment at 750°C

Fig. 5.—Variation of the $(\overline{2}01)$ reflection of the potash-rich phase of several orthoclase perthites during heat-treatment. See text.

to about Or_{80}. Thus, the nature and extent of the remixing shown by these orthoclase specimens, which are optically monoclinic and all of approximately the same bulk compositon, covers the entire range from sanidine to microcline.

is plotted as if it occurred at room temperature, i.e. at a 2θ position which is 0.20 degrees higher than measured. Errors due to adifferent thermal change in 2θ than the 0.20 degrees here assumed for all alkali

PERTHITES FROM A SINGLE INTRUSIVE OR INTRUSIVE SEQUENCE

Although the previous figures (2, 3, 4, and 5) illustrate the $(\overline{2}01)$ variation during heat-treatment, such a method of illustration when used for a wide range of compositions is extremely difficult to comprehend. Accordingly another type of illustration will be used in the hope of subtracting at least a part of the compositional and temperature effect. Figure 6 presents a generalized version of the previous figures. Five points appear to be sufficient to evaluate such a diagram (Fig. 6), namely (A) the room temperature 2θ position at the start of the run; (B) the 2θ position at 750°C at the start of heat-treatment; (C) the 2θ position at 750°C at the end of the heat-treatment; (D) the room temperature 2θ position at the end of the determination; and (E) the 2θ position which a homogeneous sanidine of this bulk composition would have (see TUTTLE and BOWEN, 1958) at room temperature. On the basis of the $(\overline{2}01)$ linear expansion measured on homogeneous alkali feldspars, the $(\overline{2}01)$ reflection

Fig. 6.—Generalized diagram showing the variation of the $(\overline{2}01)$ reflection of the potash-rich phase of a perthite during heat-treatment. The letters, A through E, indicate various 2θ positions during the heat-treatment which are used in the following diagrams (Fig. 7-14) for comparing the remixing rates of various perthitic specimens. See text.

feldspars, and other errors will affect the diagrams regardless of the method of illustration.

Figures 7 through 14 show the 2θ variation of the potash-rich $(\bar{2}01)$ phase before, during, and after

$(\bar{2}01)$ reflection of the potash-rich phase. The manner in which the $(\bar{2}01)$ reflection approaches or fails to approach the bulk composition position (item E of the foregoing paragraph is the zero or bulk-
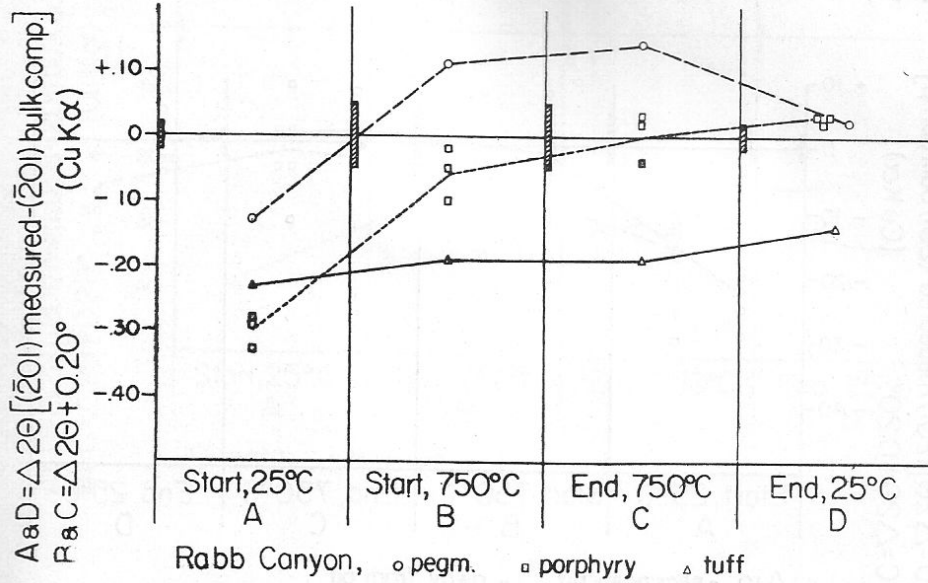
Figs. 7 through 14.—Diagrams comparing the remixing rates of alkali feldspar perthite specimens from the same intrusive or the same intrusive sequence. See text.
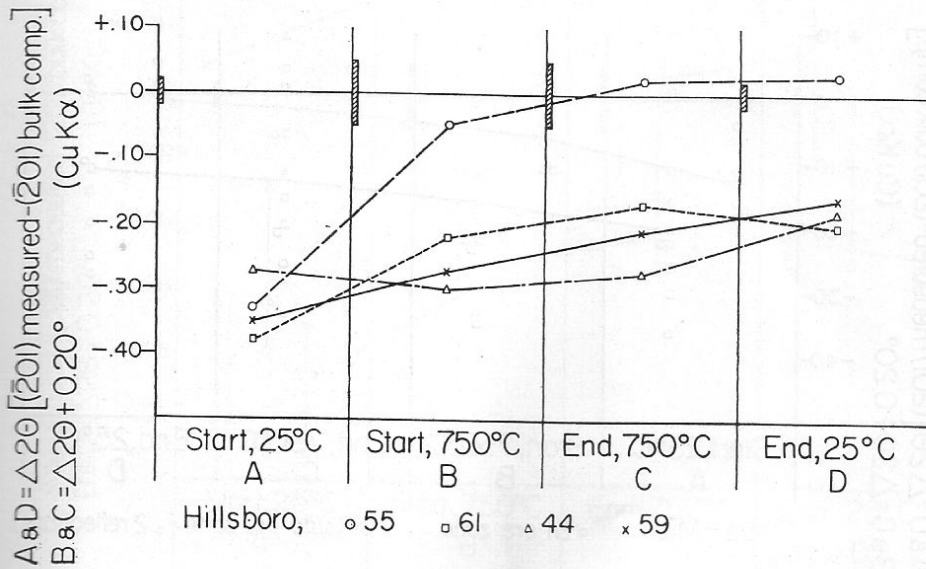
Fig. 8.

heat-treatment at 750°C, plotted as if the heating took place at room-temperature, i.e. a 2θ value of 0.20 is added to all readings at 750°C. The vertical scale is the 2θ difference between the $(\bar{2}01)$ reflection of a homogeneous sanidine of this bulk composition (based on data of TUTTLE and BOWEN, 1958) and the actual

composition position) may be seen. Along the horizontal scale each column refers to a part of the heating cycle, namely A, B, C, or D, as described in the preceding paragraph. The short heavy line on the left of each column at the zero line indicates the estimated maximum range of error in measuring the 2θ position.

The heavy line to the right of column D indicates the estimated range of error in fixing the zero 2θ position, because of the errors in compositional determination.

Remixing data for perthite samples from the Rabb Canyon sanidine pegmatite area, Grant County, New

sequence (see KELLEY and BRANSON, 1947; KUELLMER, 1960 a, p. 317) is (1) rhyolite tuff, intruded by (2) sanidine porphyry, in which (3) sanidine pegmatite lenses formed. Here the last-formed, more hydrothermal (i.e. pegmatitic and porphyritic phases)
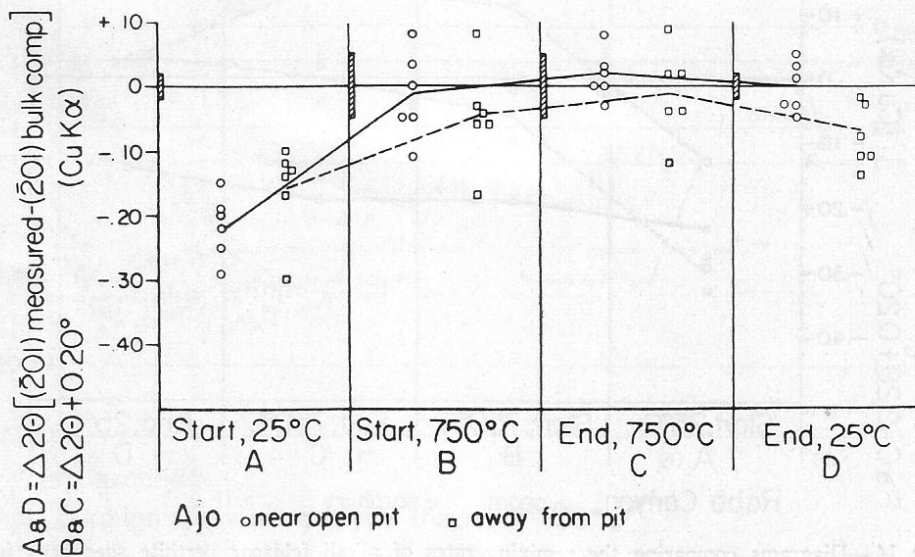

Fig. 9.
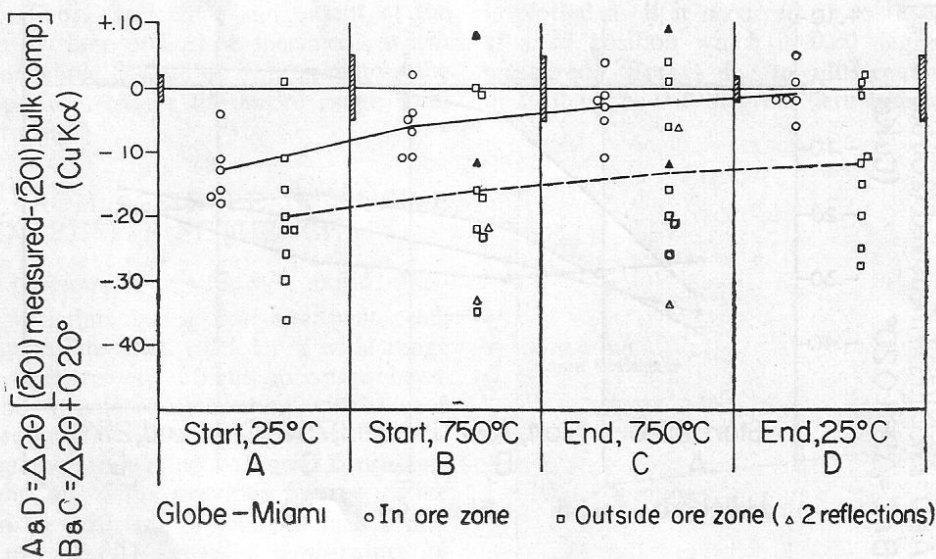
Fig. 10.

Mexico are presented in Figure 7. The moonstone sanidine from a high-temperature pegmatite remixes faster than the sanidine specimens from the sanidine porphyry, and both of these materials remix faster and more completely than a perthite specimen from the surrounding rhyolite tuff. The estimated rock

perthites, which presumably formed at lower temperatures, show the most rapid high-temperature type of remixing. Clearly, the foregoing data demonstrate that remixing is affected by additional factors other than the temperature-structural state.

Figure 8 illustrates the variation in remixing rates

for four orthoclase specimens from the quartz monzo-
nite porphyry near Hillsboro, New Mexico. One
specimen (number 55) remixes considerably more ra-

ovoid-shaped orthoclase phenocrysts (see KUELL-
MER, 1958).

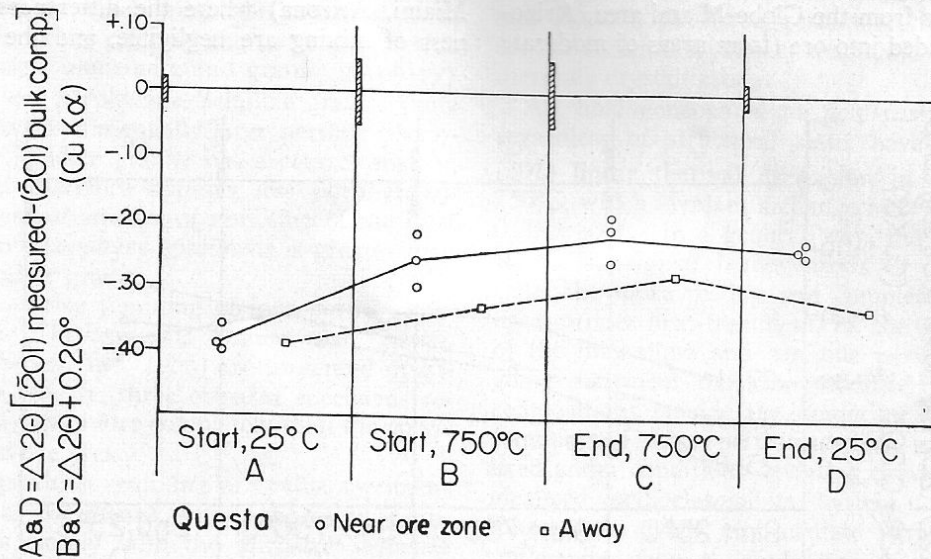Differences in the remixing behavior of specimens
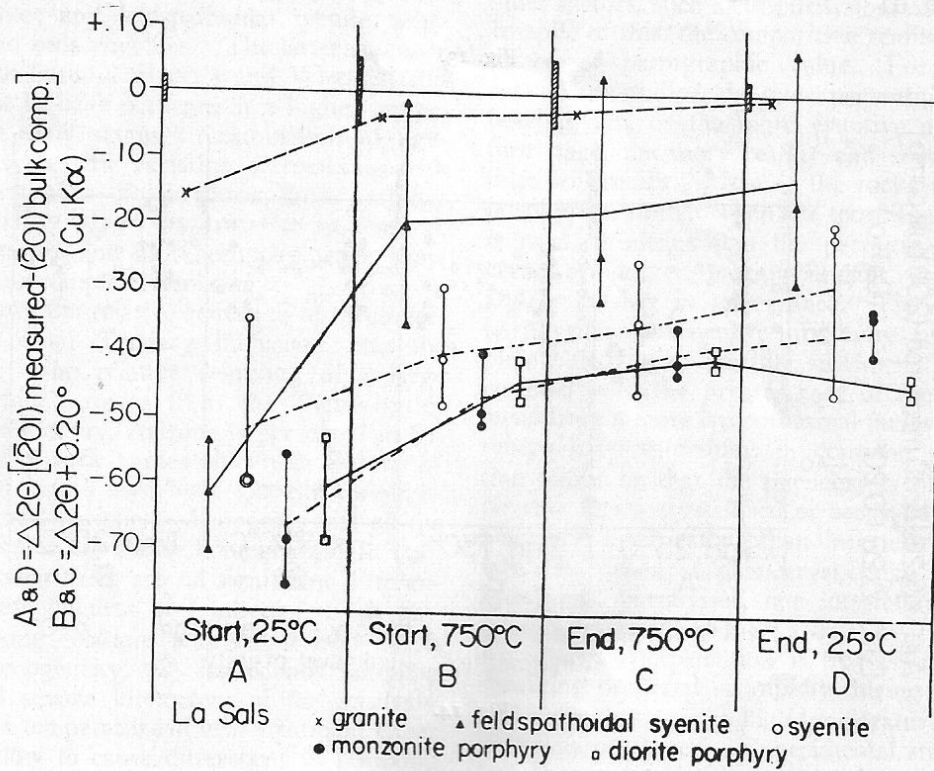

Fig. 11.

Fig. 12.

pidly and completely than the others, and indeed as
readily as most sanidines. Specimen 55 differs from
the others in that it comes from a higher intrusive
horizon, and contains conspicuously larger and more

from the Cornelia quartz monzonite (GILLULY, 1946)
near Ajo, Arizona are shown in Figure 9. Specimens
are divided into two groups, those from in or on the
edge of the open-pit mine, and those farther away.

The open-pit specimens, from the more orebearing part of the intrusive, remix more readily and completely

Figure 10 shows the remixing behavior of orthoclase perthite specimens from the Globe-Miami area, Arizona, which are divided into ore (from areas of moderate

ted in Fgure 10 by the two sets of triangles. Two of the three non-ore specimens which show complete remixing are from the Castle Dome area (near Globe-Miami, Arizona) where the differences in completeness of mixing are negligible, and the third is from
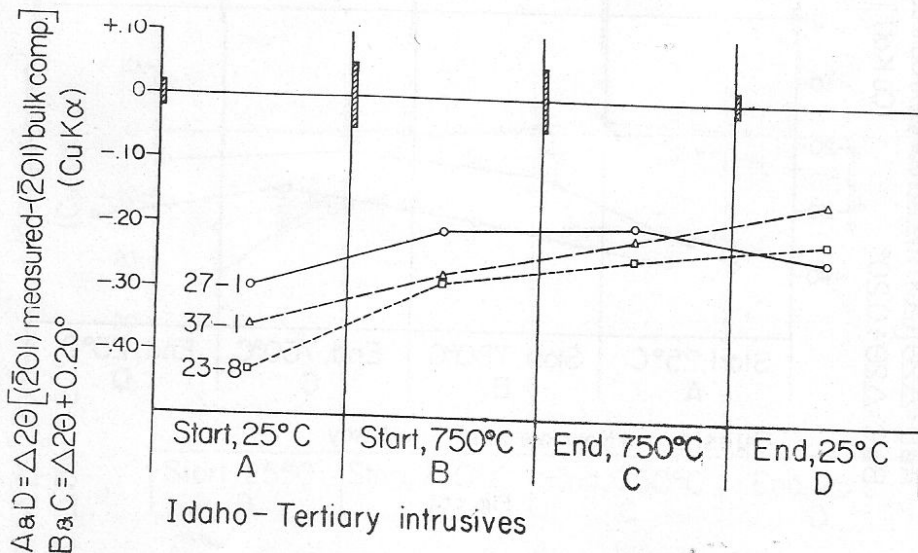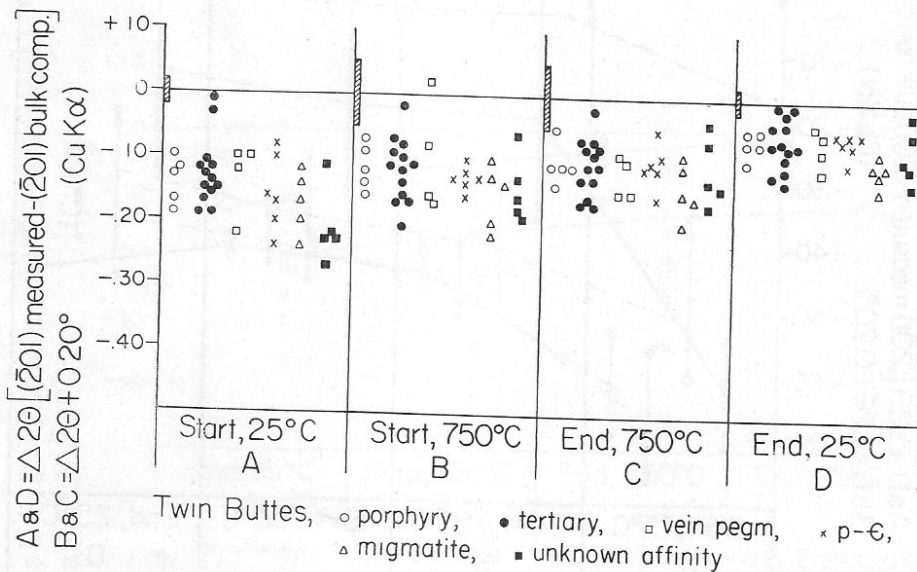

Fig. 13.

Fig. 14.

hydrothermal alteration) and non-ore specimens, based on data from PETERSON (1952). The ore specimens from this igneous sequence which includes Lost Gulch quartz monzonite, granite porphyry and Schultze granite remix more completely than most specimens from the non-ore areas. Two of the specimens from this group show two potash-rich phases which are indica-

the Inspiration mining area where the geographic separation of ore and non-ore specimens is very small. Other figures could be drawn, such as one for the Castle Dome area, which would show that the northernmost sample remixes like a sanidine, the southernmost has two potash-rich phases, and the two ore-area specimens lie somewhere inbetween, so that

the variation appears systematic with geographic position. A similar general variation with geographic position holds for the Copper Cities intrusive area. Another illustration which might be prepared is to compare the remixing rates of the more porphyritic (Lost Gulch quartz monzonite and granite porphyry) rocks and the less porphyritic Schultze granite (note that both groups contain equally large perthite phenocrysts, but the Schultze granite has a coarser matrix, in general, and therefore appears less porphyritic). Here too the general amount of remixing of the Lost Gulch and granite porphyry specimens is greater than that of the Schultze granite.

Data on the relative remixing of four perthite specimens from the Tertiary soda granite near Questa, New Mexico (SCHILLING, 1956) are presented in Figure 11. Here too, the three ore-area specimens remix more readily and more completely than the specimen from a non-ore area.

Variation of perthitic remixing of twelve specimens from the La Sal Mountains, Utah, shown in Figure 12, conforms closely with the intrusive sequence and temperature deductions as worked out by HUNT and WATERS (HUNT, 1958; WATERS, 1955). The intrusive sequence is: diorite porphyry; monzonite porphyry; syenite; and feldspathoidal syenite, aegerine granites, and soda rhyolites. The latter stages of intrusion, on the basis of HUNT's and WATERS' studies, are thought to have occurred at a higher temperature than the early stages. Examination of figure 12 shows a systematic variation of remixing with the various rock types. Furthermore, those perthites from rocks occurring late in the intrusive sequence at a higher temperature and more eruptive stage show a faster and more complete remixing.

Figure 13 shows the relative remixing of three perthite specimens from Tertiary intrusives into the Idaho batholith. The relative remixing of a large number of perthite samples from the Twin Buttes quadrangle, Pima County, Arizona is presented in Figure 14. The five rock names shown in Figure 14 are tentative field names used by J. COOPER for slightly different textural varieties. It appears that all the Twin Buttes samples are rather homogeneous in bulk composition and that there are no significant differences in rate or completeness of remixing. Such uniformity in remixing relations may result from (1) a real primary homogeneity, (2) inadequate sampling spread over 153 square kilometers of the quadrangle, (3) selecting a temperature of heat-treatment either too high or too low to cause differences in remixing rate, or (4) a complete recrystallization of the perthites.

CONCLUSIONS

Perthitic alkali feldspars from a single intrusion show a considerable compositional range (Table I). The fact that most of the orthoclases are optically homogeneous and have bulk compositional ranges which do not extend across the minimum temperature trough of the system-$NaAlSi_3O_8$-$KAlSi_3O_8$ (TUTTLE and BOWEN, 1958) suggests that these compositions are the result of a primary magmatic (including hydrothermal) crystallization.

All homogeneous alkali feldspars here measured, regardless of structural state, have about the same ($\overline{2}01$) linear thermal expansion in the range 20 to 750°C, which involves a change in 2θ (CuKα) of about $0.20 \pm .05°$. In a general way, the closer a perthite is to its original homogeneous or high-temperature state, the more readily and completely it will remix upon proper heat-treatment, on the basis of the study of the microcline and sanidine perthites. The foregoing statement must be modified to exclude bulk compositions outside the unmixing range, and metasomatic and other perthites which may have crystallized under conditions deviating considerably from the idealized orthoclase-albite system. Orthoclase perthites show every intermediate variety of remixing.

Perthites from a single intrusive or intrusive sequence show such variation in their remixing rates, that unmixing is probably considerably affected by other factors, such as impurity ions and lattice defects. In spite of this, the comparitive remixing rates appear to be of petrographic value. For mosts igneous rocks here studied, the more pegmatitic, the more ore-bearing, and/or the more eruptive or high-temperature stage, the more readily and completely the perthite will remix. Most of the rocks studied here are porphyries, so that when the term "more porphyritic" is used, it means that the perthitic feldspar phenocrysts are larger, more abundant, more conspicuous and/or fresher in appearance. The fact that more-porphyritic specimens remix more readily and completely than other perthite specimens can only be reconciled with the greater ease of remixing of specimens from a more hydrothermal facies, if these occurrences have something in common. One explanation might be that the phenocrysts of the more-porphyritic facies crystallized or recrystallized late in the magmatic cycle rather than intratellurically. Therefore two types of phenocrysts may occur in many hypabyssal porphyries, one intratelluric and another formed or re-formed at a late hydrothermal stage. An alternate explanation is that crystal growth and unmixing occurred so rapidly during the hydrothermal stage that a more high-temperature type of unmixing was preserved. Experimental studies by JAHNS and BURNHAM (1958) suggest that a late hydrothermal and rapid growth of larger crystals may readily occur. Crystals grown rapidly in a hydrothermal stage might contain more impurities and lattice defects which would affect remixing rates. The foregoing analytical prodedure may thus provide an important tool for differentiating perthitic alkali feldspars formed during various stages of magmatic crystallization.

ACKNOWLEDGMENTS

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DISCUSSION

KAMB (Pasadena):

Have you remixing data on microclines of various triclinicities?

KUELLMER (Socorro). Answer:

Todate I have no data on the remixing of microcline perthites, in which the potassium phase has less than the maximum triclinicity. A few preliminary studies of some microcline perthites suggest that the deeper and «more plutonic» (using these terms in a very general way) specimens contain perthites which remix more slowly and reluctantly than those microcline perthites from «less plutonic», or younger rocks. However, there are conspicuous exceptions to this generalization, and the number of specimens studied to date is small.

KUELLMER (Socorro). Answer to Mr. MEIER (The question was not received):

No I have not compared the matrix alkali feldspar with alkali feldspar phenocrysts from the same specimen. Some of the specimens from the Ajo, Arizona area contain no phenocrysts of alkali feldspar and matrix alkali feldspars were used. In most cases the phenocrysts, because of included impurities, required considerable microscopic sorting so that separation of alkali feldspars from a very fine-grained matrix was not attempted at this time.

Einfluss des geologischen Alters und des tektonischen Drucks auf die Art der Alkalifeldspäte

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AUSZUG

Messungen optischer Achsenwinkel werden dazu benutzt, den Zustand von Kalifeldspaeten (Sanidin-Orthoklas-Mikroklin) in jugoslawischen Gesteinen zu ermitteln. Beziehungen zwischen dem Zustand der Feldspaete einerseits und dem geologischen Alter sowie der tektonischen Beanspruchung andererseits werden aufgefunden und diskutiert.

In Jugoslavien sind granitische Gesteine verschiedenen Alters: altpaläozoische, hercynische und paläogene, vorhanden. Es ist sehr charakteristisch für diese Gesteine, dass sich die Arten der Alkalifeldspäte in ihnen ganz wesentlich unterscheiden.

In den altpaläozoischen Orthogneisen ist an Kalifeldspäten nur Mikroklin vertreten. Der Mikroklin dieser Gesteine ist teilweise gitterartig verzwillingt, teilweise homogen.

In den hercynischen Graniten, Granodioriten, Quarzmonzoniten und Syeniten sind an Kalifeldspäten

Orthoklas und gitterartig verzwillingter Mikroklin vorhanden. Uebergänge zwischen Orthoklas und Mikroklin sind in diesen Gesteinen immer vertreten.

In den Paläogenen Graniten, Syeniten, Granodioriten und Quarzmonzoniten kommt an Kalifeldspäten nur ein Na-reicher Orthoklas vor. Dieser Orthoklas zeigt immer sehr feine Albitausscheidungen, so dass er einen Krypto- oder Mikroperthit darstellt. Die Orthoklase dieser Gesteine weisen fast immer Anfangsphasen einer Umwandlung in gitterartig verzwillingten Mikroklin auf.

Diese Angaben sind am besten aus der Abb. 1, die den Charakter der Kalifeldspäte in einzelnen Gesteinen Jugoslaviens zeigt, ersichtlich.

Die oben angegebenen Daten werden sehr gut durch die Angaben über den Charakter der Kalifeldspäte in den permischen und neogenen Ergussgesteinen Jugoslaviens ergänzt. Die permischen Quarzporphyre führen an Kalifeldspäten nur Orthoklas, und die neogenen Quarzlatite, Latite, Trachyte und Rhyolithe immer einen typischen Sanidin.

Die Art der Kalifeldspäte in einzelnen Kalifeldspat führenden Gesteinsgruppen kann man sehr leicht aus den Werten des optischen Achsenwinkels ersehen.

Die Werte der optischen Achsenwinkel der Alkalifeldspäte in einzelnen Gesteinsgruppen sind in der folgenden Tabelle angeführt:
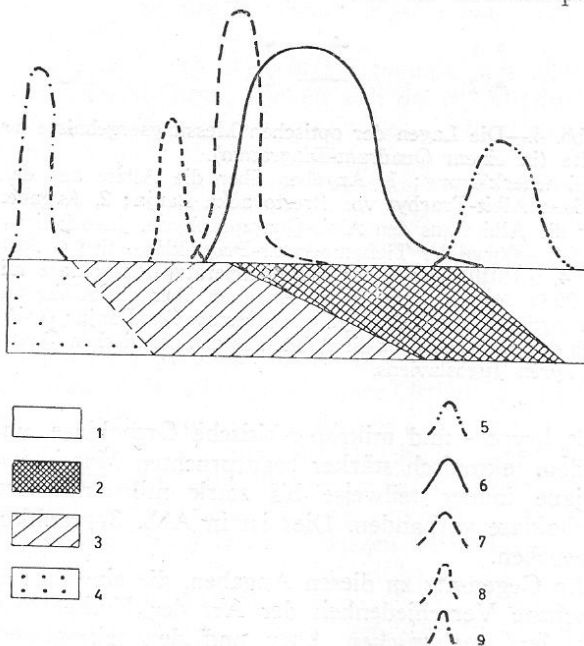

Abb. 1.—Der Charakter der Kalifeldspäte in Eruptivgesteinen Jugoslaviens.
Zeichenerklärung; 1, homogener Mikroklin; 2, lamellarer Mikroklin; 3, Orthoklas; 4, Sanidin; 5, Kalifeldspäte in den altpaläozoischen Orthogneisen; 6, Kalifeldspäte in hercynischen Graniten, Syeniten, Quarzmonzoniten und Granodioriten; 7, Kalifeldspäte in paläogenen Graniten, Syeniten, Quarzmonzoniten und Granodioriten; 8, Kalifeldspäte in permischen Quarzporphyren; 9, Kalifeldspäte in neogenen Quarzlatiten, Latiten, Trachyten und Rhyolithen.

Gesteinsgruppe	Optischer Achsenwinkel			Bemerkung
	von-bis	meistens	Mittelwert	
Altpaläozoische Orthogneise	73-80		77	wenig Angaben
Hercynische Granite, Syenite, Quarzmonzonite und Granodiorite	53-85	65-85	75	
Paläogene Granite, Syenite, Granodiorite und Quarzmonzonite	42-76	52-63	57	
Permische Quarzporphyre.	51-73	57-70	63	
Neogene Quarzlatite, Latite, Trachyte und Rhyolithe.	10-40	17-35	27	

Diese Angaben sind graphisch in Abb. 2 dargestellt. Sehr interessant ist jedoch der Einfluss des tektonischen Druckes auf die Art der Alkalifeldspäte in
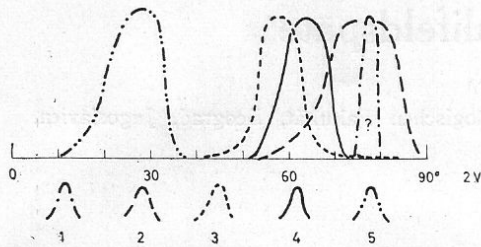

Abb. 2.—Die optischen Achsenwinkel der Kalifeldspäte in Eruptivgesteinen Jugoslaviens.

Zeichenerklärung; 1, in altpaläozoischen Orthogneisen; 2, in hercynischen Graniten, Syeniten, Quarzmonzoniten und Granodioriten; 3, in paläogenen Graniten, Syeniten, Quarzmonzoniten und Granodioriten; 4, in permischen Quarzporphyren; 5, in neogenen Quarzlatiten, Latiten, Trachyten und Rhyolithen.

den Gesteinen desselben Alters. So sind, zum Beispiel, die Alkalifeldspäte in den Gesteinen des Granodioritmassivs von Boranja (Westserbien) typische Orthoklase (Mikroperthite) mit nur Anfangsphasen einer
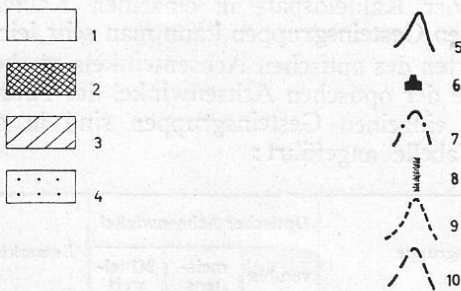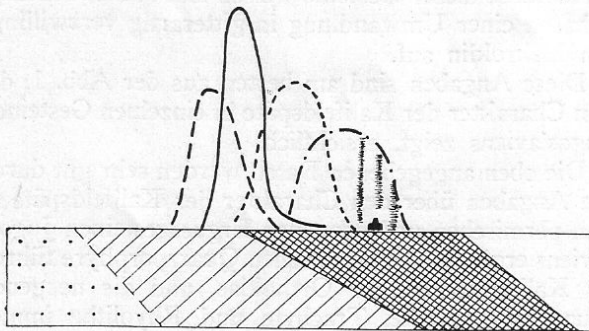

Abb. 3.—Shematische Darstellung des Einflusses der tektonischen Druckwirkungen auf die Art der Kalifeldspäte.

Zeichenerklärung; 1, homogener Mikroklin; 2, lamellarer Mikroklin; 3, Orthoklas; 4, Sanidin; 5, Kalifeldspäte in der Granodioriten und Quarzmonzoniten des Boranja-Massivs; 6, Kalifeldspäte in den protoklastischen und kataklastischen Granodioritgängen um das Boranja-Massiv; 7, Kalifeldspäte in den Graniten des Massivs von Ogražden; 8, Kalifeldspäte in den tektonisch stärker beanspruchten Teilen des Massivs von Ogražden; 9, Kalifeldspäte in den Graniten und Syeniten von Lojane; 10, Kalifeldspäte in den Graniten von Štip.

Umwandlung in Mikroklin. In den granodioritischen Gängen, die um das Massiv liegen, jedoch gleichalterig sind, und die sich von den Gesteinen des Massivs nur durch eine protoklastische und eine nachträglich gebildete kataklastische Struktur unterscheiden, findet sich fast ausschliesslich gitteriger Mikroklin. In den Graniten des Ogražden-Massivs (Mazedonien) sind die stärker tektonisch beanspruchten Teile auch viel mikroklinreicher und orthoklasärmer, als die Teile, die nicht kataklasiert sind (Tomić J., 1936). Ebenso, von zwei altpaläogenen Granitmassiven, des von Lojane und des von Štip (Mazedonien), sind in dem tektonisch fast unbeanspruchten Massiv von Štip nor-
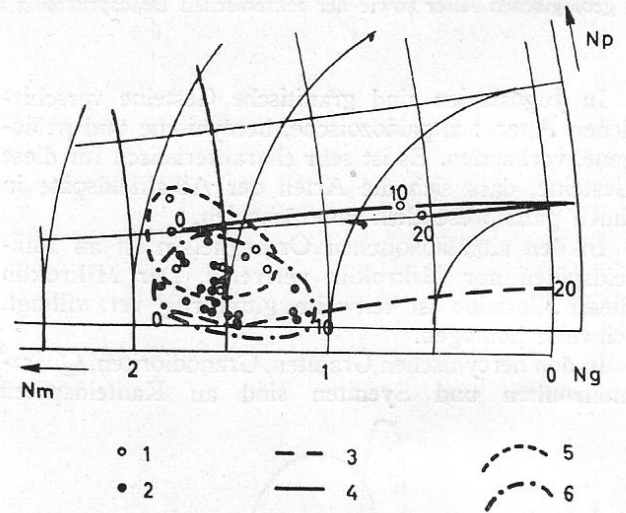

Abb. 4.—Die Lagen der optischen Messungsergebnisse der Albite (in einem Quadrant-Diagramm).

Zeichenerklärung; 1, Angaben über die Albite aus dem tertiären Albit-Trachyt von Brestovačka Banja; 2, Angaben über die Albite aus den Albit-Quarzporphyren Jugoslaviens; 3, ⊥ (010)-Kurve der Tieftemperatur-Plagioklase mit 0 — 20 % An; 4, ⊥ (010)-Kurve der Hochtemperatur-Plagioklase mit 0 — 20 % An; 5, Bereich der Angaben über die Albite aus dem tertiären Albit-Trachyt von Brestovačka Banja; 6, Bereich der Angaben über die Albite aus den permischen Quarzporphyren Jugoslaviens.

male krypto- und mikroperthitische Orthoklase, und in dem tektonisch stärker beanspruchten Massiv von Lojane immer teilweise bis stark mikroklinisierte Orthoklase vorhanden. Dies ist in Abb. 3 graphisch angegeben.

Im Gegensatz zu diesen Angaben, die eine ausgesprochene Verschiedenheit der Art der Kalifeldspäte mit dem geologischen Alter und den tektonischen Druckwirkungen, denen die Feldspäte unterworfen waren, aufweisen, können bei den Albiten aus Gesteinen verschiedenen Alters keine wesentliche Verschiedenheiten bemerckt werden. Ein Beispiel dafür sind die Albite aus den tertiären Albit-Trachyt von Brestovačka Banja (Ostserbien) und die Albite aus den permischen Albit-Quarzporphyren Jugoslaviens. In Abb. 4 wurden die Lagen der optischen Messungs-

ergebnisse aller dieser Albite in ein Quadrantdiagramm eingetragen, woraus man sieht, dass keine wesentliche Unterschiede zwischen tertiären und permischen Albiten bestehen. In Abb. 5 sind die optischen Achsenwinkel derselben Albite eingetragen, und auch hier sieht man, dass die tertiären und permischen Albite identisch sind.
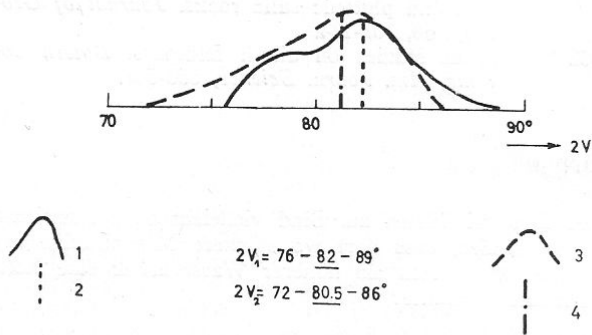

Abb. 5.—Die optischen Achsenwinkel der Albite aus dem tertiären Albit-Trachyt von Brestovačka Banja (1) und deren Mittelwert (2), sowie aus den permischen Quarzporphyren Jugoslaviens (3) und deren Mittelwert (4).

$2 V_1$ bezieht sich auf die Albite vom Albit-Trachyt; $2 V_2$, auf die Albite aus den Albit-Quarzporphyren. Die Zahlen geben das Variieren des optischen Achsenwinkels und den Mittelwert (unterstrichen).

Auf Grund der angeführten Angaben und der geologischen Stellung einzelner Massive kann man folgendes feststellen:

In einem rasch abgekühlten Sanidin, mit ungeordnetem Si/Al-Gitter, wickelt sich die Si/Al-Diffusion, wenn keine wesentliche nachträgliche Druckwirkungen oder Metamorphosen stattgefunden haben (wie es bei den Quarzporphyren Jugoslaviens meistens der Fall ist), sehr langsam ab, so dass es in mehr als 150 Mill. Jahren nur bis zur Umbildung des Sanidins in einen krypto- bis mikroperthitischen Orthoklas gekommen ist.

Bei langsamer Abkühlung, ohne Einwirkung eines tektonischen Drucks, bildet sich zunächst ebenfalls ein krysto- bis mikroperthitischer Orthoklas (wie zum Beispiel im Granit von Štip). Falls diese Gesteine auch später keinen wesentlichen Druckwirkungen unterworfen wurden, geht die weitere Si/Al-Diffusion sehr langsam vor, so dass es im Laufe von mehr als 150 Mill. Jahre nur bis zu einer teilweisen Mikroklinisierung der Orthoklase kommt. Beispiele dafür sind die Kalifeldspäte in den posttektonischen oder spättektonischen Graniten und Granodioriten von Cer (Westserbien) und Gornjane (Ostserbien), die nach ihrer Verfestigung keinen besonders starken orogenen Drucken unterworfen wurden.

Bei langsamer Abkühlung syntektonischer Granite und Granodiorite wird schon bei der Abkühlung, oder sehr schnell danach, der Orthoklas teilweise mikroklinisiert (wie zum Beispiel in den granodioritischen Gesteinen des Boranja-Massivs in Westserbien). Es scheint sehr wahrscheinlich, dass sich dieser einmal eingetretene Prozess leichter fortsetzt, so dass bei analogen syntektonischen hercynischen Intrusionen, auch wenn sie keinen stärkeren (wie z. B. das Granodioritmassiv von Stražanica in Westserbien) oder keinen besonders starken [wie z. B. das Granit-Massiv von Bujanovac in Südserbien (DIMITRIJEVIĆ M., 1958)] tektonischen Druckwirkungen später unterworfen wurden, der Orthoklas vollkommen mikroklinisiert wurde.

Nachträgliche tektonische Druckwirkungen beschleunigen, ebenso wie die Drucke bei der Abkühlung, die Si/Al-Diffusion und führen während sehr grosser Zeiträume nicht nur zu vollkommener Mikroklinisierung der Orthoklase, sondern auch zur Homogenisierung der gitterigen Mikrokline.

Insgesamt betrachtet kann man sagen, dass die Si/Al-Diffusion ein sehr langsamer Prozess ist, der bereits für die Anfangsphasen der Mikroklinbildung aus Orthoklas sehr grosse, über 100 Mill. Jahre lange Zeiten braucht. Die tektonischen Druckwirkungen beschleunigen diesen Prozess und beeinflussen ihn ganz wesentlich.

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DISCUSSION

KAMB (Pasadena):

Haben Sie in Ihren Proben röntgenographisch bestimmt, ob es sich um Orthoclas oder Mikroklin handelt, oder haben Sie das nur optisch untersucht?

KARAMATA (Beograd). Answer:

Die Alkalifeldspäte aus paläogenen Granodioriten usw, wurden optisch und röntgenographisch (LUKOVIĆ, S., 1960); die aus den herzynischen und vorherzynischen granitoiden Gesteinen nur optisch untersucht.

LAVES (Zürich):

Sie schreiben des öfteren stärkere Mikroklinisierung er-höhten Druckeinflüssen zu. Sind vielleicht auch Anzeichen dafür vorhanden, dass dort wo stärkere Mikroklinisierung beobachtet wird, auch ein höherer Wasserdruck eine Rolle gespielt haben könnte?

KARAMATA (Beograd). Answer:

Der Einfluss des Wassergehaltes im Magma auf die Art der Alkalifeldspäte, die bei der Kristallisation entstehen, wurde nicht besonders berücksichtigt, weil die paläogenen Granodiorite usw. immer Hochplutone sind, in denen die Wassergehalte ähnlich und relativ klein waren, während es bei den älteren (herzynischen und vorherzynischen) granitoiden Gesteinen sehr schwer ist, den primären Wassergehalt im Magma abzuschätzen.

The amphibolite-granulite facies transition reflected in the mineralogy of potassium feldspars

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ABSTRACT

The two-feldspar geothermometer indicates that the amphibolite to granulite facies transition takes place at temperatures slightly above 500°C in the areas studied by the author. Granulite facies rocks show a range in temperature between 500-600°C; and amphibolite facies rocks are in the 400-500°C interval. 720-780°C is indicated as the crystallization temperature for anatectic granites in granulite facies rocks, whereas late red granitic veins in the amphibolite facies seem to have crystallized at about 300°C.

Measurements of variation in the $2 V_x$ and in the (131) doublet separation indicate that monoclinic (or pseudomonoclinic) orthoclase is stable in granulite facies rocks, while microcline is stable in amphibolite facies rocks.

Apart from temperature, variation in H_2O pressure, and in the confining rock pressure may influence the relation between order-disorder transformation of potassium feldspar and metamorphic grade.

INTRODUCTION

An understanding of the physical and chemical conditions of feldspar formation, the mutual relations between the feldspar minerals and their structural variations, would go a long way towards solving some of the most intricate problems of petrogenesis; particularly those connected with the orogenic basement rocks: gneisses and granites. In all these rocks feldspar is a major constituent.

Structural and chemical work in the feldspar group of minerals during roughly the last 10 years indicates that the feldspars may be used to explain diverse petrological aspects of metamorphic rocks, especially those of the amphibolite and granulite facies.

Aplications of experimental and theoretical data on the feldspar minerals to the study of metamorphic rocks: gneisses and granites. In all these rocks feldof authors (Barth, 1956; Dietrich, 1960; Heier, 1956, 1957, 1960; Heier and Taylor, 1959 a and b; Taylor and Heier, 1960).

This paper discusses some variations in the symmetry of alkali feldspars, and in the relations between alkali feldspar and plagioclase within the PT interval usually asigned to amphibolite and granulite facies.

TEMPERATURE OF FORMATION OF THE ALKALI FELDSPARS.

Barth (1934, 1951, 1956) proposed to use the distribution coefficient;

$$k = \frac{\text{mol fraction of albite in alkali feldspar}}{\text{mol fraction of albite in plagioclase}}$$

as a geological thermometer for rocks where K- feldspar and plagioclase coexist in equilibrium. The coefficient depends chiefly upon temperature but is also influenced by the chemical environment and, as shown by Yoder et al. (1957) and Bowen and Tuttle (1950), by pressure.

A discussion of factors other than the above which may interfere with the validity of the thermometer is given by Dietrich (1960).

It is obvious that only the most recent lowest temperature at which equilibrium existed between the feldspar phases is recorded. This is important with respect to an application of this thermometer to genetic considerations of problematic igneous vs. metamorphosed sedimentary rocks, as a magmatic temperature can be cited as evidence for a magmatic origin while a submagmatic temperature cannot be cited as evidence against an ultimate magmatic origin (Dietrich, 1960, p. 46).

Despite the limitations of the two-feldspar geothermometer the fact remains that the temperature indicated by rocks so far checked do fall in the ranges into which they would be put by most petrologists on the basis of other considerations.

In theory it would seem that the two-feldspar geothermometer would be especially suitable for recording temperature variations in rocks of granulite facies and the higher part of amphibolite facies. Barth (1956) suggested that the geothermometer could be used to advantage for rocks in which "plagioclase is in the range 10-30 An. and the alkali feldspar in the range 10-30 Ab.". These are the typical compositions of feldspars in rocks from the said facies. The feldspars in this facies range are also typically free of

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secondary alterations which are characteristic of the lower grade metamorphic rocks, and also of plutonic igneous rocks approaching granitic composition.

Thus HEIER (1960) investigated an area where amphibolite facies gneisses are succeeded by similar gneisses in granulite facies and determined temperatures in the 400-500°C range for amphibolite facies rocks, with temperatures increasing towards the metamorphic boundary. A minimum temperature of 300°C is indicated by a young red granitic vein which is genetically not directly related to the country rock gneisses.

The analogous gneisses in granulite facies yield temperatures in the interval 510-570°C, and still higher temperatures (570-600°C) are reached by some porphyroblastic hypersthene monzonites within this area.

Magmatic temperatures are indicated for another type of monzonites, and for some red granites within the granulite facies area. These rocks were assumed from field considerations to be of an igneous origin.

The red granites are especially interesting in this connection and are plotted on the projection of the quaternary system $NaAlSi_3O_8$ (Ab)-$KAlSi_3O_8$ (Or)-$CaAl_2Si_2O_8$ (An)-H_2O at 5000 bars water pressure (Fig. 1). The dominant minerals are quartz and alkali feldspar mesoperthite. Some independent albite grains are typically present. Biotite and iron ore are accessory minerals (ca. 2 %).

It is interesting that the plots of the granites on Fig. 1 cluster around the cotectic curve defining the composition of magmas yielding simultaneously alkali feldspar and plagioclase as primary phases upon cooling. The one granite which plots at an appre-

ciable distance away from the curve (1, Fig. 1) is the only one in which mesoperthite is the only feldspar phase. This indicates that the rock composition is closely identical to that of the crystallizing magma.

The 750 and 800°C isotherms are indicated on Fig. 1. If the rocks crystallized under physical conditions similar to those for which the diagram was constructed the crystallizing temperatures should be between 725 and 800°C.

In the case of no. 2, Fig. 1, the alkali feldspar was separated from the rock and analysed (x, Fig. 1). The coexisting albite is of composition An 12. Using the two-feldspar geothermometer a temperature of 780°C was derived. As read from Fig. 1 this temperature should be about 725°C at 5000 bars. A lower pressure would increase the temperatures in Fig. 1. (3000-4000 bars was suggested by BARTH (1952) for the confining rock pressure during granulite facies metamorphism). The similarity between the two temperatures is quite satisfactory.

A temperature of about 500°C for the amphibolite-granulite facies transition is in agreement with the temperature asigned to this facies transition by a number of authors (BARTH, 1952; RAMBERG, 1952; ROSENQVIST, 1952). In conjunction with this it is appropriate to note that DIETRICH (1960) using the same method found temperatures somewhat less than 400°C for some banded gneisses with the mineral parageneses corresponding to epidote amphibolite facies.

Possible use of the chemical feldspar thermometers.

The distribution law of Nernst furnishes the theoretical basis for the two-feldspar geothermometer. The distribution law is showed to be valid only for ideal dilute solutions, and is not strictly applicable to the distribution of albite between coexisting potassium feldspar and plagioclase. Theoretically the distribution of elements present in only trace amounts, and having crystal chemical properties which make substitution in the two types of feldspar lattices roughly equally feasible, would make a better geothermometer. Very little work has been carried out along this line. This is partly because of the more difficult mineral separation involved, and partly because of the more complex analytical technique. BARTH's geothermometer has the advantage of being generally usable from the standpoint that equipment necessary for analyses is available in most geological institutions.

Some indicative work has been done by HEIER (1960). He found for a restricted number of rocks that the distribution of Sr, Ba and Pb between coexisting feldspars shows similar trends as the albite geothermometer (Fig. 2).
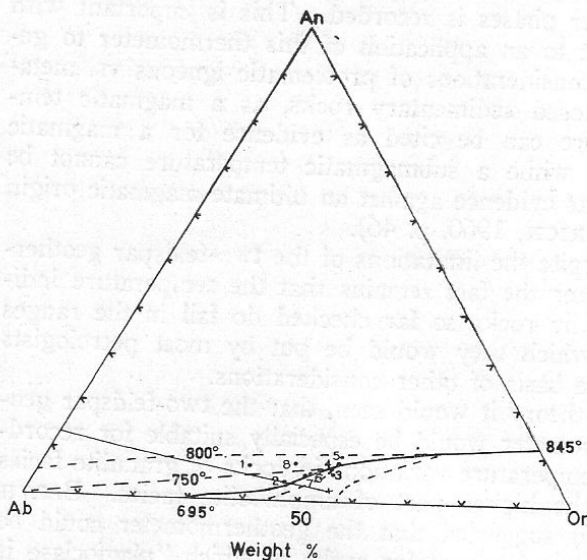

Fig. 1.—Normative Or+Ab+An of some red granites occurring with granulite facies rocks on Langøy, Northern Norway, plotted on the projection of the quaternary system $NaAlSi_3O_8$(Ab)-$KAlSi_3O_8$(Or)-$CaAl_2Si_2O_8$(An)-H_2O at 5000 bars water pressure (YODER et al., 1957). x, separated alkali feldspar from no. 2; tieline connects it with the coexisting plagioclase (optically determined).
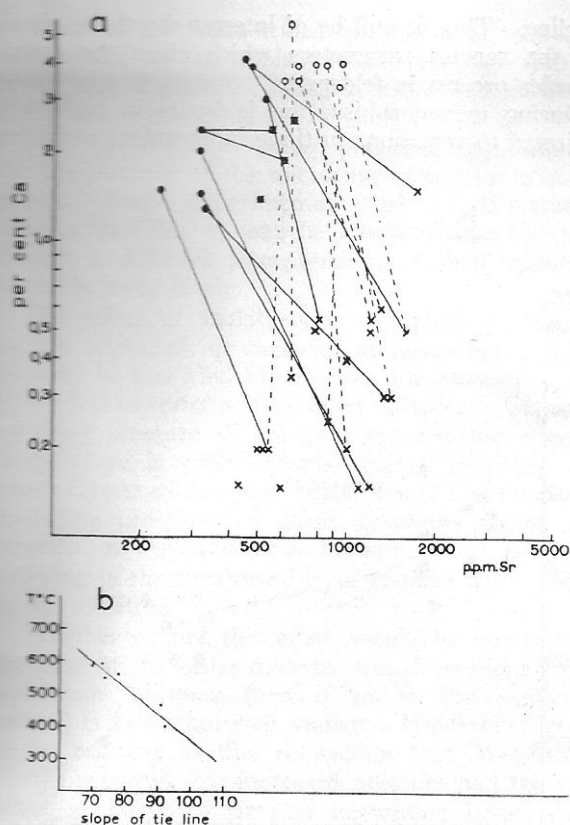
Fig. 2 a.—Relations between Ca and Sr in potassium feld-spars (X), plagioclase (o), and rocks (·) from Langøy, Northern Norway. (■) mesoperthitic alkali feldspars. Thin lines connect coexisting minerals and/or rocks.

Fig. 2 b.—Slope of tieline between plots of Ca/Sr in plagioclase and Ca/Sr in potassium feldspar plotted vs. temperature of formation of the potassium feldspar as determined by the «albite geothermometer», (BARTH, 1956).

SYMMETRY VARIATIONS OF POTASSIUM FELDSPARS IN PROGRESSIVE METAMORPHISM

The work by GOLDSMITH and LAVES (1954) on hydrothermal heat treatment of microcline showed a monoclinic phase to form at about 500°C after 500 hrs. heating. A temperature of 500°C is considered by several authors to be close to the temperature of the amphibolite-granulite facies transition. This then would make a study of the symmetry variations in potassium feldspars in this PT range look especially rewarding.

HEIER (1957) discussed the phase relations of potassium feldspars in metamorphism and showed "that the symmetry of potash feldspars is affected by the degree of rock metamorphism in such a way that rocks with mineral combinations corresponding to the granulite facies or the higher part of amphibolite facies contain potash feldspars which appear monoclinic".

Further he found that the transition "monoclinic→ triclinic potash feldspar seems to take place at PT conditions a little below the transition between granulite and amphibolite facies", and "when the PT conditions fall below those of high grade amphibolite facies, the complete ordering of the potash feldspars seems to take place within a narrow PT field. Thus, for rocks of undoubted amphibolite facies, nearly all ranges of triclinicities may be found."

A monoclinic potassium feldspar, or orthoclase, was defined as a potassium feldspar appearing optically monoclinic and showing no splitting of the (131) reflection on X-ray powder diagrams. [The (131)-doublet reflection was used by GOLDSMITH and LAVES (1954) as measure of deviation from monoclinic symmetry; the triclinicity (Δ) defined as 12.5 (d (131)-d ($1\bar{3}1$)]. This is also the definition of an orthoclase used in the subsequent discussion.

HEIER (1960) studied the symmetry variations of feldspars from rocks in the amphibolite-granulite facies range.

The ordering of the potassium feldspar structure would result in an increase of the $2 V_x$, other conditions being equal. The amphibolite facies rocks studied by HEIER (1960) have potassium feldspars with $2 V_x$ never less than 55-60°, and with a spread between 55-85°. In potassium feldspars from granulite facies rocks the $2 V_x$ has not been found to exceed 50-55°, and is typically between 45-50°. Especially in the amphibolite facies gneisses $2 V_x$ has been found to vary considerably even within the same crystal. A variation between 55-80° in the same grain has been recorded. Such variation seems to be characteristic of intermediate microclines (GOLDSMITH and LAVES, 1954 b).

Fig. 3 a shows the relationship between $2 V_x$ and temperature of formation as determined by the two feldspar geothermometer. Only progressively metamorphosed rocks wich have not been subjected to any retrograde metamorphism are considered on Fig. 3 a.

The same series of feldspars was also examined by the X-ray powder method. The feldspars from the granulite facies rocks showed no separation of the (131) doublet, and are characterized by a somewhat broad and diffuse single reflection.

Some of the feldspars from the amphibolite facies rocks also showed a single diffuse reflection; these had the lowest $2V_x$ in the group, and microcline twinning was not seen in thin sections. However, most of the amphibolite facies feldspars have large triclinicity values. Fig. 3 b shows plots of triclinicity vs. temperature of formation. If this figure is compared with Fig. 3 a it seems that 2V is more sensitive to symmetry variations than is triclinicity; i.e., the 2V undergoes a rather marked change before the splitting up of the (131-$1\bar{3}1$) reflections is noticable. The latter shows no splitting up above 470°C, but

directly below that a high triclinicity obtains. Intermediate triclinicities are rare and it seems that ordering of the potassium feldspars takes place within a narrow PT field. The dotted line on Fig. 3 a and b indicates that approximate maximum ordering of alkali crocline. Thus it will be of interest shortly to consider the various parameters which affect the order-disorder process in feldspars.

During metamorphism the feldspars in rocks are subjected to variations in three independent variables
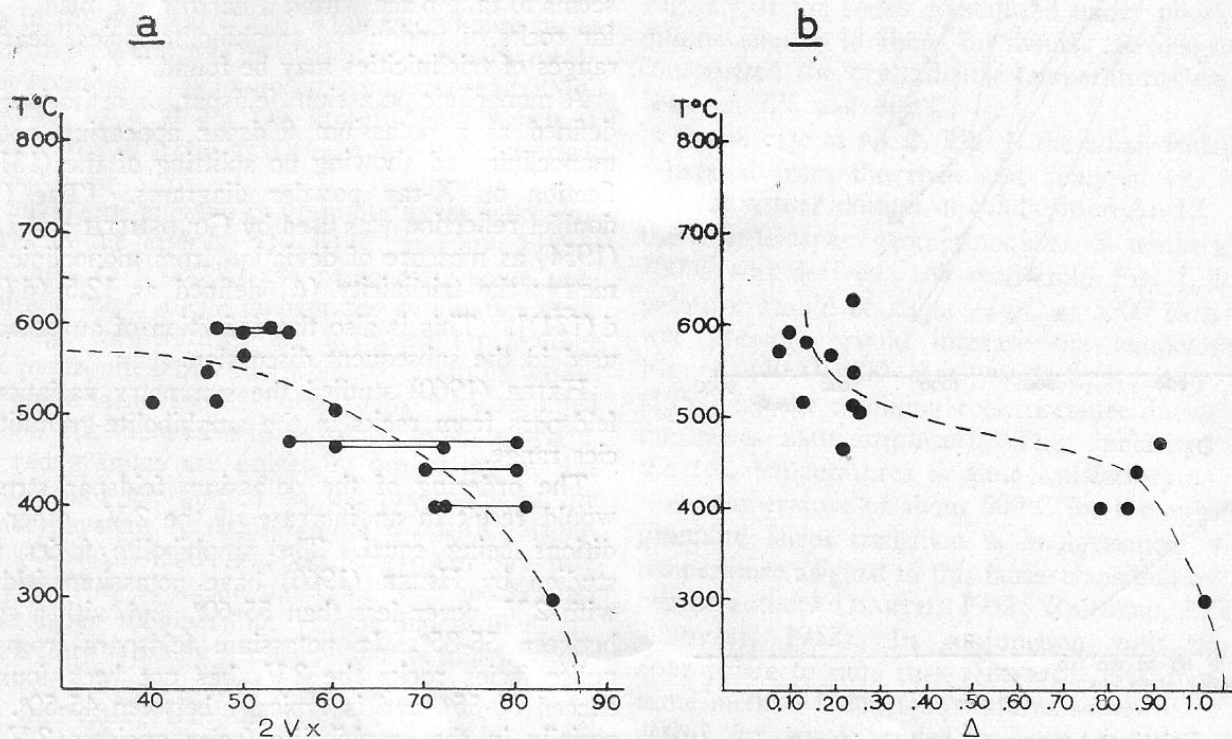

Fig. 3 a.—Relationship between $2V_x$ and temperature of formation of potassium feldspars from progressively metamorphosed rocks from Langøy, Northern Norway.

Fig. 3 b.—Relationship between triclinicity (Δ) and temperature of formation of potassium feldspars from progressively metamorphosed rocks from Langøy, Northern Norway.

feldspars was achieved at temperatures a little less than 300°C. Based on other evidence BARTH (1959) concluded that the temperature at which disorder becomes apparent in the potassium feldspar structure is around 300°C.

FACTORS INFLUENCING THE ORDER-DISORDER TRANSFORMATION

The study of potassium feldspars in metamorphic rocks by HEIER (1956, 1957, 1960) indicates that the microcline-orthoclase transformation in regional metamorphic rocks defines closely the transition between granulite and amphibolite facies. This conclusion agrees with findings from elsewhere (WILSON, 1954; PARRAS, 1958) but cannot be claimed to have a general validity. HOWIE (1955) reported the potassium feldspars from the Madras charnockites, which are granulite facies rocks, to be dominantly microcline perthites, even though closer examination often showed them to be intermediate between orthoclase and mi-

acting on the system; P (pressure), T (temperature), and X (composition).

In the preceeding discussion only variations in T have been considered, and without doubt increasing temperatures favour the disordered orthoclase structure.

The influence of variations in composition is more difficult to ascertain. The temperature of the gradual transition from microcline to orthoclase (i.e., from triclinic to monoclinic symmetry) will probably increase with increasing content of sodium. However, this point is probably irrelevant to this discussion as available analyses of potassium feldspars from different granulite facies areas show them to be chemically closely similar.

Water is included in the X parameter, and variations in water pressure may be significant. As far as the stability of orthoclase in granulite facies areas is concerned its influence may be twofold.

(1) The temperature of the transition amphibolite facies-granulite facies is dependent upon the water pressure. A low water content would lower the tem-

perature of the facies transition, and thus microcline may remain as the stable feldspar structure into the lower part of granulite facies in rocks with an abnormally low water content.

(2) Variations in water pressure may influence the temperature of the microcline-orthoclase transformation. Some experimental work by Goldsmith and Laves (1954 a) may be interpreted in this way, though a different interpretation of their results is probably more likely.

The effect of variations in confining pressure is usually neglected, or regarded as insignificant in discussions of this kind (apart from the associated catalytic effect of water and/or other volatiles). Generally speaking pressure should have the opposite effect of temperature in order-disorder transformations. Recently Crowley and Roy (1960) found that increasing formation pressures on sheet structures caused contraction of the structures brought about by Al-Si ordering in the tetrahedral layer coupled with a defect in the structure.

Whether or not this effect would be operative in the case of the order-disorder transformations in the potassium feldspars (and if so to any significant extent) is as yet not well known. However, it seems to be relevant in this connection that MacKenzie (1957) reported that increased pressure had the same effect as increased time in prompting better Al-Si ordering in hydrothermally synthesized albites.

Thus a number of factors may possibly influence the order-disorder transformation in feldspars, and it is not strange that otherwise similar rocks possess feldspars with some structural differences. As disordered feldspar structures are metastable in surface rocks the post metamorphic history will obviously be of extreme importance for the metastable retainment of a disordered structure.

SOME OTHER CONSIDERATIONS

The tendency for increasing disorder of the structure with increasing degree of metamorphism (i.e., increasing temperature) harmonizes with all general tenets. However, in studying the electrostatic charge distribution in the alkali feldspars, Ferguson et. al. (1958) stated "that an enhanced degree of Al-Si ordering need not necessarily be associated with greater stability in the potassium feldspars". They interpreted their data as suggesting that in the series "maximum microcline" to orthoclase stability increases as order decreases; i.e., orthoclase is the stable low temperature form. MacKenzie and Smith (1959) have questioned the validity of this statement both on theoretical and empirical grounds without their criticism being entirely accepted by Ferguson et al. (1959). A crucial point to concider seems to be the statement of Ferguson et al. (1958) that the presence

of sodium during cooling is essential to the formation of a microcline. MacKenzie and Smith (1959) imply this to mean that the presence of sodium in the lattice actually favours the formation of a microcline perthite over an orthoclase perthite and they point to available published data which show orthoclase perthites to be typically considerably higher in sodium than microcline perthites, and thus contradict this view. Fig. 4 also shows the microclines from am-
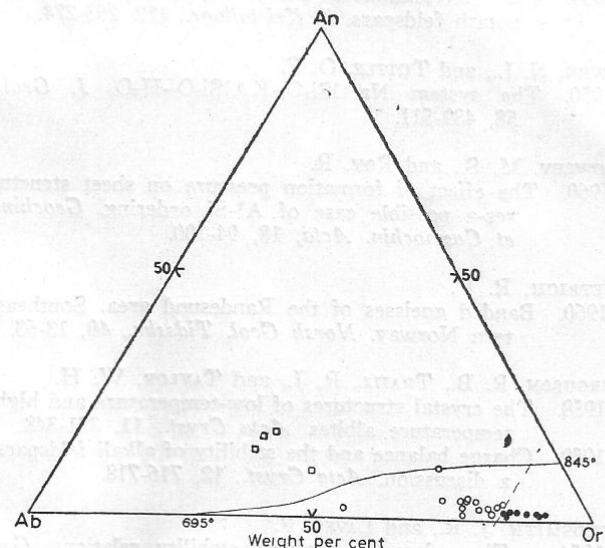
Fig. 4.—Alkali feldspar compositions from Langøy plotted on the projection of the quaternary system NaAlSi₃O₈(Ab)-KAlSi₃O₈(Or)-CaAl₂Si₂O₈(An)-H₂O at 5000 bars H₂O pressure (Yoder et al., 1957). Dashed line separates between feldspars from amphibolite (right) and granulite (left) facies rocks. □, mesoperthitic alkali feldspars.

phibolite facies rocks studied by Heier (1960) to be characteristically lower in sodium (albite) than the orthoclase of granulite facies.

Ferguson et al. (1959) state that the implication made by MacKenzie and Smith (1959) about the higher sodium contents in orthoclase perthites is not strictly relevant to their hypothesis. Their discussion of the K-Na-feldspars was meant to involve the separation of the cooling range into two regions; "in the upper, the Si, Al distribution (and so the geometry of the crystal structure) may vary in accordance with the K-Na ratio and with the cooling rate; in the lower, migration of K and Na ions may continue although no further change in the Si, Al distribution can take place".

Although this statement may be difficult to dispute as far as feldspars from gradually cooling igneous rocks are concerned the data from rocks examined by Heier (1960) where feldspars from progressively metamorphosed rocks are considered, are clearly at variance with their hypothesis. All data show that increasing temperatures stabilize the disordered orthoclase structure, and increase the amount of sodium which may be incorporated in the structure.

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DISCUSSION

HOWIE (Manchester):

I have taken X-ray powder patterns of about 30 potassium feldspar from charnockites from Madras and elsewhere and find that in almost all cases the feldspar in these granulite facies rocks is a microcline. In only one case was orthoclase found, and this was in a hornblende-biotite-bearing variety, perhaps nearer to the amphibolite facies. How would you explain this discrepancy with your results?

HEIER (Houston). Answer:

The odd behaviour of the K-feldspars from the Madras charnockites is mentioned and discussed in the prepared paper. Because of time this was not read at the meeting. I will, however, refer to the paper, and add that Dr. KUNO from Japan later informed me that my data agree with what they have found in Japan.

DIETRICH (Blacksburg):

How do you propose to account for lack of correlation between 2 V and obliquity (triclinicity, Δ·value)?

J. V. SMITH (Chicago):

Concerning the lack of correlation between 2V and Δ observed by HEIER, I should like to say that 2V depends on short range order and Δ on long range order. Factors such as Ca probably cause variability in the domain structure that results in lack of correlation between long and short range order.

HEIER (Houston).   Answer to DIETRICH:

Question was answered by Dr. SMITH.

MACKENZIE (Manchester):

One of the plagioclase feldspars on Fig. 4 seems to be unusually rich in the orthoclase molecule. Does Dr. HEIER consider that this feldspar was ever one homogeneous feldspar phase?

HEIER (Houston). Answer:

The feldspar in the plagioclase field on Fig. 4 are considered as originally having crystallized as a homogeneous phase and having formed metasomatically (today they are mesoperthites). The reason for this is in that they are depleted in Rb which only can be explained to result from geometrical reasons (HEIER and TAYLOR, 1959, *Geochim. et Cosmochim. Acta* 15, 284-304).

The structure of anorthite

by C. J. E. KEMPSTER, H. D. MEGAW, and E. W. RADOSLOVICH
(University of Cambridge)

ABSTRACT (*)

Anorthite, $CaAl_2Si_2O_8$, has an ordered structure with 8 formula units in the unit cell, which is built up from 4 albitoid subcells. The structure was derived in two stages from trial coordinates given by the albite structure: in the first stage, reflections with h + k even (l even or odd) were considered, giving the «base-centred approximation», and in the second stage those with h + k odd, which were systematically weaker, were included to give the true primitive lattice. At each stage the signs of the systematically weak reflections were first found by supposing them due to Ca contributions only, and then corrected during refinement by inclusion of the other atoms (effectively a heavy-atom thechnique). No assumptions were made about (Si, Al) distribution; in the later stages, these atoms were distinguished by their size, the standard deviation of the mean tetrahedral bond length being about 0.012 Å.

It is found that Si and Al alternate, each O atom having one Si and one Al neighbour. The order is perfect, within the limits of experimental error, which are fairly narrow. There are differences of coordinates of all atoms between the four subcells, most marked for Ca; three Ca's have 7 neighbours in the range 2.3 to 2.8 Å, while the fourth has 6 only.

Geometrical differences between subcells related by a body-centring translation cannot be attributed to difference of (Si, Al) occupation, and are in fact larger than between subcells with different (Si, Al) occupation. They must be explained as a mechanism of reducing strain in the (Si, Al)-O framework, and attention is called to their importance. The conspicuous difference of sites for Ca in the four subcells follows as a consequence. Since these atoms make the largest contributions to the difference intensities they provide sensitive indicators of the subcell differences without being physically important in relation to their cause.

DISCUSSION

KAMB (Pasadena):

How does the degree of agreement between calculated and observed structure factors for the «a» reflections compare with that for the subsidiary «b», «c» and «d» reflections?

MEGAW (Cambridge). Answer:

It is not easy to make a clear comparison for two reasons: (a) the errors due to incomplete refinement in the F_c's of the difference reflections are by no means random, but tend to make F_c systematically low, so that adjustments to the scaling factor are needed; (b) the experimental errors in the F_o's are relatively much larger for the weak difference reflections than for the strong main reflections. The R-factor for the difference reflections was always larger than for the main reflections, but decreased in the same way and much more rapidly. In the final stages the two were not calculated separately.

KAMB (Pasadena):

Does your primitive anorthite structure provide bond-angle data in support of the idea that the puckering-deformation of the structure improves the Si-O-Si angle over that of the «average» structure?

MEGAW (Cambridge). Answer:

We have not yet calculated the bond angles for anorthite but hope to do so.

We do not expect to find any easy answer to the question of stability. Too little is yet known about the dependence of bond angles on electrostatic valence and repulsive force. There is in general a wider range of Si-O-Si bond angles between different O's in the same feldspar than between comparable O's in different feldspars, which suggests that each atomic site must be considered separately, and we cannot say which changes of bond angle are in the direction of lower energy.

I would like to emphasise that I do not think it is *only* the Si-O-Si angles which must be considered; each angle, and each length, in the structure contributes to the energy, and the resultant structure represents a balance between them. I called particular attention to the Si-O-Si angles because they are often disregarded; if they were completely free the whole framework would be more flexible than I believe it to be.

I should also like to make it clear that in anorthite the «average structure» has no physical meaning, whatever it may have in materials where it represents the solution obtained using all the available diffraction evidence. Primitive anorthite is a perfect structure (to the best accuracy to which we can work) and the «average structure» here is merely a convenient fiction for handling the refinement by successive approximations.

Structure of «body-centred anorthite»

S. Chandrasekhar, S. G. Fleet and H. D. Megaw

(University of Cambridge)

ABSTRACT (*)

«Body-centred anorthite» is a plagioclase feldspar of composition about $Ab_{20}An_{80}$ with a 14 Å c-spacing and systematic absences for reflections with $h + k + l$ odd. It has been refined by Fourier methods, from three-dimensional data, taking as independent starting points the structure of albite and the structure of anorthite; both methods give results which are in substantial agreement.

The observed electron-density distribution can best be explained as an average of two arrangements resembling, but not identical with, the two halves of the anorthite cell related by the vector $1/2\,a + 1/2\,b + 1/2\,c$. This implies that the true unit cell consists, like anorthite, of four different albitoid subcells, but that there are out-of-step domains, related by this vector, with dimensions so small that the difference reflections not common to the two are smeared out and lost by diffraction broadening.

There is (Si, Al) segregation of the same kind as in anorthite, i.e. there is a perfectly regular alternation of Si-rich and Al-rich sites. At the present stage of refinement, however, the segregation appears to be less complete than in anorthite.

DISCUSSION

Kamb (Pasadena):

Is it not possible that an incorrect assignment of signs to the subsidiary reflections could give rise to the observed failure to resolve the elongated peaks in the «average» structure by a simple splitting into two subcells?

Megaw (Cambridge). Answer:

There seems no possible way in which incorrect assignment of signs can produce the effect. We have tested all the possibilities as far as we can.

In any case, if the two-subcell structure were the true one, it would raise a difficulty in explaining why there is no evidence of a discontinuity between it and the four-subcell structure of pure anorthite. We did not use this argument in deriving the structure, but it is important nevertheless.

Gay (Cambridge):

I would like to comment on the occurrence of the body-centered anorthite whose structure is described. This material is what would be called «a transitional anorthite», though by neglecting the diffuse (c) reflections you will get a body-centred structure. With regard to true body-centred anorthite, I would like to point out that it does not seem to exist as a low temperature mineral, for the diffuse (c)

reflexions occur right down to 50 % An. Body-centred anorthite may exist as a high temperature form, but that is in accord with the present picture.

Megaw (Cambridge). Answer:

I agree with Dr. Gay that this is not a true body-centred anorthite; I used the name, in inverted commas, with some hesitation, because it has been used of this material in the past. I also agree with him in thinking that true body-centred anorthite does not exist at low temperatures, but not for the reason given in his remark. The appearance of diffuse-c reflections down to about 50 % An is, I believe, a consequence of the structure of the e-plagioclases, which is essentially different from that of the b-anorthites. The disappearance of diffuse-c reflections with increasing Na content is almost complete before the transition at which 'b' reflections are replaced by 'e'; their subsequent reappearance is irrelevant. On the other hand there is no suggested structural change which could account for the increasing diffuseness of 'c' reflections and still culminate in a truly body-centred structure; this is why I think the body-centred structure does not occur. Our material was as nearly an 'absent-c anorthite' as we could get; it did not show any obvious diffuse-c reflections on Weissenberg photographs with long exposures, but only a few weak streaks. Since it was thus empirically very nearly an end-member, I do not like to call it 'transitional'. The existence of the streaks is in agreement with our interpretation in terms of a four-subcell structure like that of primitive anorthite, but with antiphase domains.

The structure of the intermediate plagioclase feldspars

by Helen D. Megaw
Cavendish Laboratory, Cambridge, England.

ABSTRACT

The ideal plagioclase structure has a unit cell made up of 18 albitoid subcells, 16 of which belong to one or other of the four types found in anorthite, and are arranged so as to give extensive blocks of anorthite structure. Sets of stacking faults on several different fault planes occur with probabilities depending on the composition, and have the effect of displacing the systematically-weak intensity maxima («difference reflections») from their ideal lattice positions, in three dimensions. These results, with a detailed quantitative description of the stacking faults, are deduced directly from the diffraction effects, without the use of any hypotheses about atomic «ordering». With the assumption that faults in annealed material have their origin in site mistakes which necessarily occur at non-stoichiometric compositions, it is then possible to make some generalisations about the (Si, Al) and (Ca, Na) distributions throughout the series, with the help of the observed resemblances to anorthite. It is shown that the geometrical or «puckering» effects noticed in anorthite plays a more fundamental part than does the (Si, Al) ordering, though the latter is also important.

The theory provides a complete quantitative explanation of the positions of the intensity maxima and the variation with composition of all three reciprocal-space coordinates; it explains qualitatively their variation of breadth and intensity with composition and with heat treatment; and it shows the relationship of the intermediate plagioclases to high and low albite on the one hand, to low anorthite («primitive anorthite»), high anorthite and «bodycentred anorthite» on the other. It opens up possibilities for further understanding of the potash feldspars in their relation to the soda feldspars.

In the time at my disposal I can only give an outline of this work; the full paper is to appear shortly in the Proceedings of the Royal Society. Here I shall have to skip all the mathematics and much of the detailed argument, concentrating on the conclusions, but I would like to emphasize that the arguments *do* exist.

The materials dealt with here are those feldspars lying in the range between roughly 25 % An and 75 % An which show "extra reflections". These have been studied extensively by many workers, including Taylor; Cole, Sørum and Taylor; Laves and Goldsmith; Gay; Gay and Bown. The present work aims to give an explanation of the observed results.

The experimental facts are briefly as follows. The b-type reflections of primitive anorthite (h + k odd, l odd) are replaced in these plagioclases by symmetrically-placed pairs of about the same intensity, which are called "e"; and other pairs, which are called "f", appear symmetrically about the main or a-type reflections (h + k even, l even). The vector joining the points in reciprocal space corresponding to he "e" pair increases and changes direction with increasing albite content; the corresponding vector for the "f" pair is always parallel to it and of twice the length. These results are usually described in terms of the reciprocal-space coordinates of "e"-reflections with respect to one or other of the types of primitive anorthite reflections as origin. The spots are sharp down to about 50 % An, becoming more diffuse towards 25 % An.

It is convenient to define new axes by the transformation

$$a_o = a$$
$$b_o = 1/2 (a + b)$$
$$c_o = 3/2 a + 1/2 b + c$$

where a, b, c, define the conventional unit cell of albite. Then, of the new coordinates of "e", $(\delta a)_o$ varies from $0°$ to $40°$, while $(\delta b)_o$ remains constant at $40°$ and $(\delta c)_o$ remains nearly constant at $0°$ (with a slight trend which we can ignore until later). Hence it is possible to draw a new reciprocal lattice with sides $1/9\ b_o^*$ and $1/2\ c_o^*$ as in Fig. 1, carrying all the observed reflections. It corresponds to a direct cell of dimensions $9\ b_o \times 2\ c_o$. The doubling of c_o is necessary to explain the continued existence of the (diffuse) c-type reflections. It is also found later to help in explaining the intensities quantitatively.

We have now to explain the systematic absence of some of the reflections to be expected from this reciprocal lattice. Of the sequence of 8 points in the direction of the b_o^*- axis between two a-type reflections, the 1st and 8th are "f", the 4th and 5th "e", but the others are absent. This regularity in reciprocal space can be explained by postulating a suitable regularity in direct space in the arrangement of subcells within the true cell (1). (Each subcell is closely similar to a primitive unit cell of albite.) We consider first a 4-element line grating, each element consisting of a pair of slightly different subcells 1, 2; and next a 2-element grating, each element consisting

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(1) The absences along $(c)_n = 180°$ are explained, like the diffuseness of the c-type reflections, by antiphase domains caused by faulting on $(010)_n$.

of four subcells 1, 2, 3, 4, the separation of the elements being $2b_o$ in both cases.   If the transforms of these
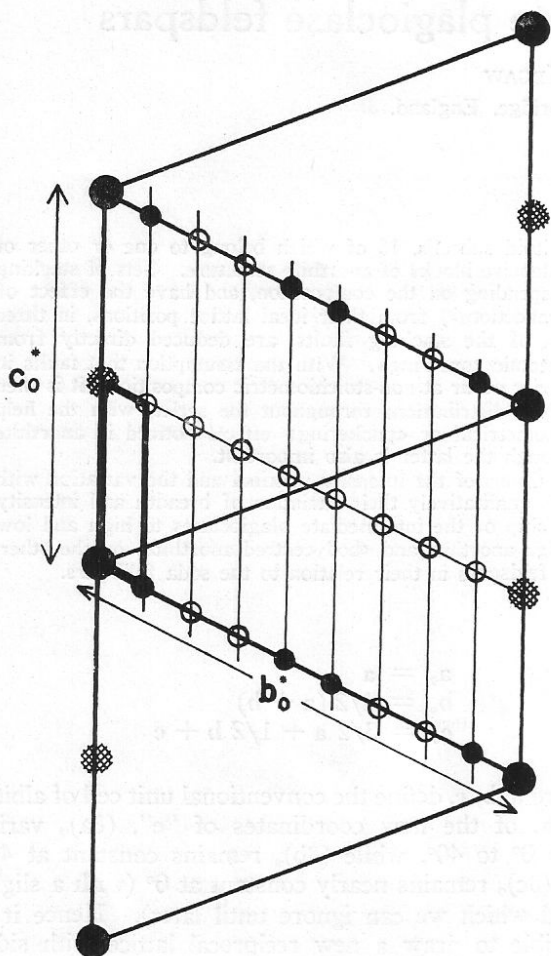

Fig. 1.—Reciprocal lattice of plagioclase structure.

gratings are constructed and sampled at points corresponding to the maxima of a lattice of spacing $9 \, b_o$, the
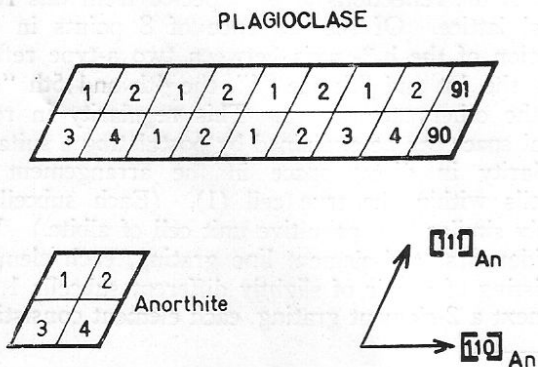
PLAGIOCLASE

Fig. 2.—Unit cell of plagioclase structure, and comparison with anorthite.

heights of the 2nd, 3rd, 6th and 7th maxima are low. A combination of the two arrangements, as in Fig. 2, is still better.   It can be shown quantitatively that this set of subcells can explain (i) the unobservably low values of the intensities at reciprocal lattice points between "e" and "f", (ii) the independent variation of the intensities of "e" and "f", (iii) if subcells 1, 2, 3, 4 are identified with those in anorthite, the resemblance of the "e" intensities to the b-type intensities of anorthite.

Table I.

CALCULATED AND OBSERVED INTENSITIES.

Calculated intensities $= P^2 F_c{}^2 + Q^2 F_b{}^2$, where F_c, F_b are functions of the differences of the subcells (F_d neglected) and P, Q are functions of the reciprocal-space coordinate.

Order of maximum	P²	Q²	Observed intensity	
			Near 75 % An	Near 50 % An
1 — «f»	8.3	0.1	Strong	Absent
2	0.3	0.7	Absent	Absent
3	1.0	3.0	Absent	Absent
4 — «e»	0.4	32.1	Medium	Medium

The outline of this calculation is shown, slightly over-simplified, in Table 1.   The intensity is here given as the sum of two terms, each itself a product of two factors.   One, the trigonometrical function P or Q, is determined wholly by the transform, i.e. by the sequence of subcells.   Hence, where P and Q are small, the intensity can never be large, whatever the value of the other factor F_b or F_c.   These, however, are themselves rather small, as they are structure factors depending on the *difference* between the subcells; their magnitude of course varies with their position in reciprocal space.

To explain the movement of reciprocal-space maxima with composition we must postulate the existence of stacking faults.   The observed movement in the $a_o{}^*$ direction depends on stacking faults parallel to $(100)_o$. It can be shown mathematically that it is proportional to the frequency of occurrence of faults; and that the observed values require a "slip vector" of $-2b_o$.   This is illustrated in Fig. 3.   If the faults are fairly regularly distributed the spot remains sharp; if they are random with a high average frequency it becomes broadened.   The observed sharpness at compositions above 50 % An indicates regularity.

The value of $(\delta c)_o$ does not remain exactly zero. This can be explained by assuming a second set of stacking faults, parallel to (001), intersecting the $(100)_o$ set and independent of them.   Here again the slip vector is $-2b_o$.   The effect is smaller than that on $(100)_o$, but seems unmistakable.

There is probably a third intersecting set on $(010)_o$, less well defined, with slip vector c_o, responsible for the diffuseness of the c-type maxima.

So far, the argument, except for one point, has been entirely restricted to lattice effects and no evidence has been introduced which could give informa-

subcells 90 and 91 (cf. Fig. 2), where a change of step must occur. Secondly, even when stacking faults occur the same alternation is preserved except near the bridging subcells. This gives a reason for the somewhat unexpected result that the slip vector for faults on both $(100)_o$ and (001) is $-2b_o$, a result which
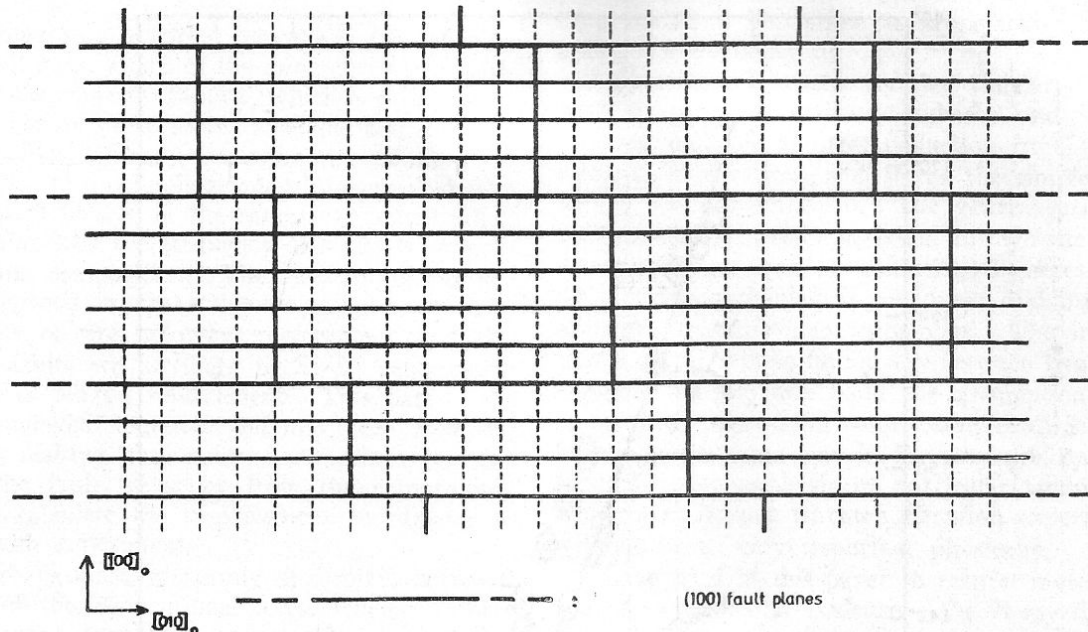

Fig. 3.—Illustration of fault planes on $(100)_o$.

tion about individual atoms within the repeat unit. It may be thought of as the counterpart, in the study of periodic structures, of a phenomenological treatment in thermodynamics.

To learn anything about the atomic positions we must know the *individual* intensities, not merely generalisations referring to the "e" or "f" class as a whole. Here we have available the piece of evidence mentioned as an exception in the previous paragraph —the fact that the "e" intensities are very like those of the b-type reflections of anorthite. From this it has been possible to deduce that 16 of the 18 subcells closely resemble those of anorthite (as illustrated in Fig. 2) and since the structure of anorthite is fully known we can go on to consider the structure of the plagioclase in more detail.

In anorthite, the Si and Al atoms alternate perfectly. This means that in two of the four subcells the occupation of particular sites is reversed with respect to the other two. Rows of subcells parallel to c_o are alike in their Si/Al occupation, and are reversed with respect to adjacent rows. In the plagioclase structure, two important effects are noticeable. Firstly, even where the sequence of subcells differs from that of anorthite the Si/Al alternation of anorthite is retained everywhere except at the two "bridging"

was derived geometrically and with no forethought what its effect on the Si/Al arrangement would be, and which therefore provides an interesting confirmation of the physical importance of the arrangement with perfect Si/Al alternation.

We now consider the bridging subcells. If they contain only Si, while the other 16 subcells have the exact 1:1 ratio, the composition is $Ab_{2/9}$ $An_{7/9}$, i.e. 78 % An. This fits so well with the not-very-well-defined composition at which the "e" reflections give way to b-type and $(\delta a)_o$ extrapolates to zero that we take it as the composition of *ideal low plagioclase*.

Whether the ideal structure is ever actually achieved is uncertain. It seems likely that there are stacking faults on (001) and $(010)_o$ even at this composition. But it is certainly useful, as in much of the felspar work, to have a well-defined ideal structure to which to refer actual materials.

We have still to ask the question, why and how do stacking faults depend on the composition? I believe we can answer that in general terms, which may be of wider application than just to the felspars.

Consider a material whose unit cell contains a number of atoms which, while similar chemically, are not related geometrically. Then they will not necessarily behave identically in the way they allow of replace-

ment by guest atoms. For some the probability of replacement may be negligibly small. For others, where it occurs readily, the consequences may differ. In some cases the guest atom may be accommodated with very little disturbance. In some, the disturbance will be greater; it may even give rise to compulsory interchange of Si and Al on certain neighbouring

sites, but will not spread far beyond them —it is so to speak a closed-circuit effect. But in some the disturbance will not be levelled out within the dimensions of the subcell. Instead it serves as a nucleus for the development of a fault plane, which is in fact a region of two-dimensionally perfect periodicity, fitting on to, but not an exact repeat of, the parts
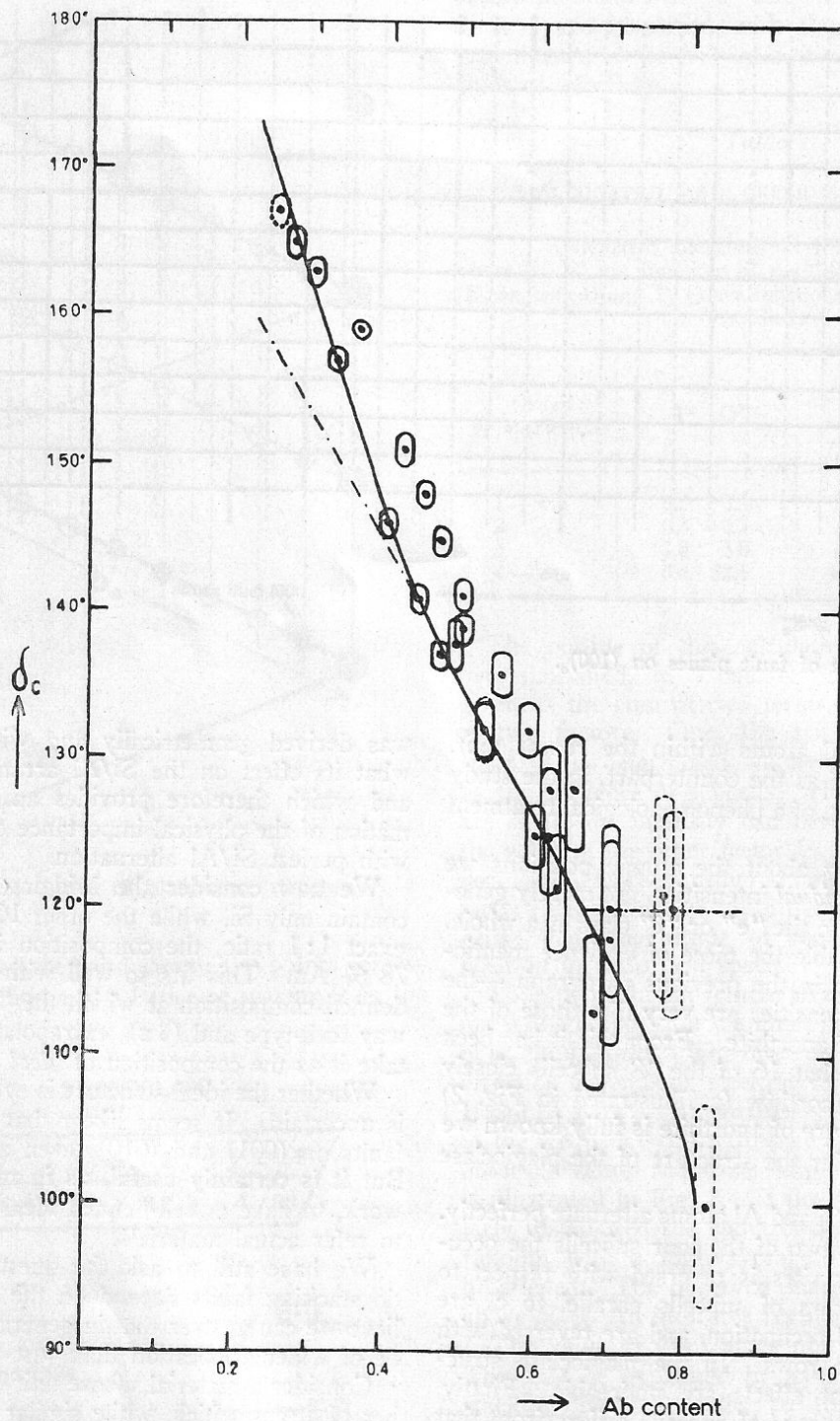

Fig. 4.—Comparison of calculated values of γ_c (full curve) with experimental observations. (Dot-dash lines show calculated values if only $(100)_o$ faults were present.)

of the perfect structure on either side. One site-mistake per cell on the appropriate site may be enough to give rise to a fault plane. But the fault plane itself is *not* the result of a tendency to disorder: the site-mistakes may initially be disordered, but the growth of fault planes from them is in fact a stage in an ordering process, which requires suitable annealing conditions.

We assume as a working hypothesis that all sites which admit guest atoms of the same chemical species do so with the same probability, which is proportional to the number of guest atoms available and hence to the composition. Some sites may not admit guest atoms at all. (All crystallographically-equivalent sites will of course behave in the same way statistically.) This explains why the frequency of faults is proportional to the composition. The constant of proportionality depends on what value we assign to the relative number of sites allowing replacement, and also on which faults we attribute to Si/Al replacement and which to Na/Ca replacement. This part of the work is somewhat tentative and may need modification. But making reasonable assumptions we can calculate the fault frequency from the composition, and hence calculate the displacement coordinates to compare with experiment.

It is perhaps most interesting to display the result in terms of the conventional axes, when all three reciprocal-space coordinates vary with composition. For δa and δb, the calculated curve is nearly a straight line, lying close to the experimental points but rather towards one side of their somewhat scattered field, an effect which may plausibly be ascribed to incompleteness of annealing. For δc, shown in Fig. 4, the effect of the (001) fault is to make the curve bend upward at the anorthite-rich end. Below 50 % An, another kind of stacking fault may set in, with slip vector b_0, but the increasing diffuseness of the reflections makes it impossible to say whether this gives a significantly better fit.

To sum up, I would say that the large unit cell with its array of anorthite subcells and its set of stacking faults is a direct deduction from the experimental observations and seems the simplest model which will explain them. The general principle of the dependence of stacking faults through site mistakes on composition (and on annealing) is necessary, but the detailed mechanism is not known and any suggestions are tentative and incomplete. The interpretation is an attempt to find a way between two opposite dangers: on the one hand the assumption that all atoms of the same kind —for example, all Si atoms— behave in the same way in the structure, and on the other an over-emphasis on particular atomic details which may happen to catch attention experimentally without being very important physically.

I have tried in this paper to restrict myself to one line of experimental evidence —the X-ray diffraction effects observed in these particular materials. Consideration of other work in the light of the conclusions reached here is left to a later paper.

DISCUSSION

J. V. SMITH (Chicago):

Having been privileged to see the manuscripts of Dr. Megaw's papers on this subject, I should like to congratulate her on her success in dealing with this very difficult problem. Secondly, I should like to point out that last week I saw electron diffraction patterns of the CuAu I alloy phase showing exactly the same type of (e) and (f) non-Bragg reflexions as those found in intermediate plagioclase. Thirdly, I should like to ask if it is possible to combine the separate slip vectors proposed by Dr. Megaw into a single irrational plane on a statistical basis. I do not like the idea that these slip vectors are independent, and wonder whether strain energy might link them, thus giving rise to a chemical and temperature control. Fourthly, I wonder if Dr. Megaw has any ideas for explaining the optical effect known as labradorescence.

MEGAW (Cambridge). Answer:

I also have seen the very pretty work of Pashley and Glossop on the Cu-Au alloy, and while the resemblances of some features are certainly interesting I think they are not strictly analogous.

It is possible to describe the system of fault planes and slip vectors in a number of different ways, as I have shown in my full-length paper published elsewhere; I would not hesitate to say that the kind of description suggested by Professor Smith is impossible, but I doubt if it would be useful. The single plane would change direction with composition; and also the interpretation of the effect in terms of atomic bonds and atomic environments might be much more confusing. I am sure that the idea of surface strain energy is relevant, but it will take us nowhere unless it is expressed in atomic terms, and as yet we have no theory which will take us very far towards formulating it quantitatively.

I am afraid I cannot say anything about the origin of labradorescence.

GAY (Cambridge):

We have heard this afternoon an account of a theory to explain one of the most difficult problems in X-ray crystallography. With few exceptions, it seems possible to explain all the facts, but I will feel happier when there is some direct evidence for the existence of stacking faults. This can be attempted by electron microscopy, and I hope that some work of this kind will be done in the near future.

GAY (Cambridge):

I would like to question the idea that the spread of the experimental results of the satellite displacements can be

correlated with incomplete annealing of the specimen. All the experimental evidence that we have suggests that the position of the (e) spots in reciprocal space is determined by the composition of the plagioclase and is unaffected by heat treatment; the intensities of the satellites are, of course, changed by heat treatment.

MEGAW (Cambridge). Answer:

Dr. GAY is right in saying that the attribution of the spread of the experimental results to incomplete annealing is unjustified. It can however be seen that the departures from the theoretical values indicate a reduced frequency of $(100)_0$ faulting. This might arise if impurity atoms such as K caused local segregation of Si in sites which do not give rise to faults, thus reducing the amount available for entry into fault-producing sites. The effects are in any case fairly close to the experimental limits of error, and explanations at this stage cannot be much more than guesses.

Effects of temperature and composition in the plagioclases and other felspars

by HELEN D. MEGAW

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ABSTRACT

An attempt is made to discuss energy relations in the feldspars in terms of their structures. The recognition of displacive transitions introduces new factors to be taken into consideration. Quenching from above the transition temperatures will tend to produce antiphase domains, in which the difference between subcells is still recognisable. Annealing may or may not bring about «ordering» of atoms. «Ordering» is not a simple phenomenon, and the kind of ordering is influenced by the displacive transition. At any general composition, numerous different ordered structures may be postulated, many of which will have nearly equal energies, but the detailed distribution of energy values will depend strongly on the geometry of the framework. With the help of these ideas, the empirical results available are used to sketch a rough phase diagram for the plagioclase feldspars. The discussion is extended to include the potassium and barium feldspars.

This paper is an attempt to put together the facts about structure reported in the earlier papers of this series, and to see how they are related to other knowledge of felspars.

It seems that there are two independent effects to be considered, the effect of Si/Al ordering which is well known and has received much attention, and what I may call the geometrical puckering effect, which has hitherto hardly been taken into account but which it now appears is of primary importance.

The puckering effect occurs in a continuously-linked structure, and is characterised by the fact that successive groups of atoms are nearly but not exactly repeated by some symmetry element, the exact repetition being achieved after a fixed number of operations of the element, most commonly two. When the symmetry element in question is a lattice translation —the case with which we are concerned here— the result is that the unit cell is doubled in that direction, and consists of two subcells which are nearly but not quite identical. Fig. 1 illustrates this: the linkages are essentially similar but the whole framework is slightly distorted so that it takes two units to make a true repeat. The effect may occur in two or more directions simultaneously. It is not peculiar to silicates, and it does not depend on ordering relationships between chemically-related atoms; it can happen in perfectly ordered chemical compounds. We have examples in materials like $NaNbO_3$ and $CaTiO_3$, where the structural units are octahedra linked by their corners. The most obvious and important example for the present discussion is anorthite, where the unit cell consists of four albitoid subcells, and the pairs with opposite Si/Al arrangements resemble each other much more closely geometrically than do the pairs with identical Si/Al arrangement.

One can suggest a reason for such a puckering effect. Suppose you were required to build a model of a structure given ideal values not only for the interatomic distance and the bond angles at Si but also for the bond angles at O. You would probably

Length of edge of true cell

Length of edge of subcell

Fig. 1.—Illustration of a hypothetical puckered structure.
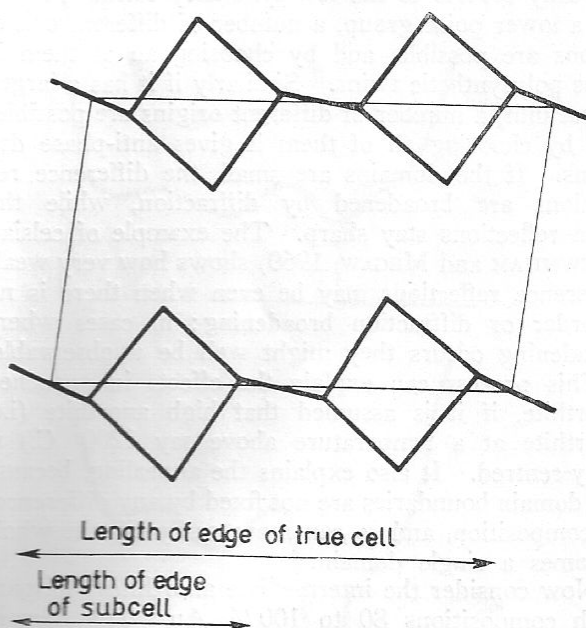
find yourself unable to do it without distorting some of the lengths or angles or both. You would need to rely on the elastic properties of your materials to give certain limits of tolerance to the values specified. If, however, you were allowed to double the cell edge before making an exact repeat, you could manage with less tolerance at some or all of the atoms. In

the actual structure the bond lengths and bond angles, and also what corresponds to their elastic tolerance, will be controlled by the wave functions of the atoms and the local electrostatic field. In the present state of knowledge it may not be possible to calculate them theoretically. But if we recognise that the bond angles at oxygen are not infinitely soft, we can see why large-cell structures may be energetically favourable at low temperatures.

At higher temperatures the increased energy of thermal vibrations is likely to lead to greater tolerance in the hinge angles, which may perhaps be associated with an increasing degree of ionic character. This allows a transition from the puckered structure to a straightened-out structure with a smaller number of subcells. This is effectively an increase of symmetry even if the space group remains unaltered.

It seems that this straightening out is what happens in anorthite about 1200° C (1). Probably at high temperatures it becomes truly body-centred. It is generally believed that no Si/Al rearrangement takes place in anorthite below the melting-point, and a straightening-out transition of this kind would not require any. It is a displacive transition, in which there is no diffusion of atoms to new sites.

Now displacive transitions cannot easily be quenched in; at the lower temperature, the material automatically reverts to the low-symmetry form. If this has a lower point group, a number of different orientations are possible, and by choosing all of them it gives polysynthetic twins. Similarly if it has a larger repeat unit, a number of different origins are possible, and by choosing all of them it gives anti-phase domains. If the domains are small, the difference reflections are broadened by diffraction, while the main reflections stay sharp. The example of celsian (NEWNHAM and MEGAW, 1960) shows how very weak difference reflections may be even when there is no disorder or diffraction broadening; in cases where broadening occurs they might well be unobservable.

This process can explain the effects in quenched anorthite, if it is assumed that high anorthite (i.e. anorthite at a temperature above say 1200° C.) is body-centred. It also explains the annealing, because the domain boundaries are not fixed by any differences of composition, and so can move easily till the whole becomes a single domain.

Now consider the intermediate anorthites: felspars with compositions 80 to 100 % An. The domain boundaries will contain sites which are different in energy from those within the domain; they may be better for Si, or they may be worse, but in any case they will favour a particular Si/Al arrangement. Hence movement of the boundaries to anneal out domains is sluggish compared with pure anorthite where

no diffusion was needed. Thermodynamically there will still be a tendency to have the boundaries spaced as regularly as possible; but the best laboratory annealing conditions may not be as good as those in nature.

Let me return to consideration of the puckering effect, whose importance I want to emphasise. I believe that it exists throughout the plagioclase series from anorthite to high albite (I leave low albite out of consideration for the present). The evidence for it is as follows.

1) Continuity of macroscopic properties throughout the series, and lack of any well-marked break.

2) Effects found in the study of the e-plagioclases, notably the resemblance of 'e' intensities to the b-type intensities of anorthite and the need for 4 kinds of subcell in order to explain the relative values of 'e' and 'f' intensities.

3) Comparison of structural details. At present it is only the Ca/Na atom whose changes are sufficiently conspicuous to be informative. It has been seen how in 'body-centred anorthite' the average structure had each Ca/Na replaced by two half atoms, each half atom being recognisably close to one of the four Ca positions of anorthite. In some uncompleted work on a high-temperature andesine of 7 Å spacing (KEMPSTER, 1957) there are indications that each Ca/Na atom should be replaced by four quarter atoms. There is a continuous movement of the four positions with composition which can be extrapolated so as to end at the two Na positions in high albite (assuming that this too can be interpreted as an average structure).

It is of course assumed in this argument that the presence of four quarter Ca/Na atoms in the average structure implies also the presence of four geometrically different pieces of Si/Al-O framework; the framework is physically more important than the Ca/Na atom in determining the stability, but the Ca/Na atom is a more sensitive and easily-observed indicator.

All this suggests that the puckering effect is, at least to a first approximation, independent of any question of Si/Al order or even of Si/Al ratio. It is there whether the Si and Al are ordered or disordered —geometrical differences due to different Si/Al arrangements, which must of course exist, are, according to this argument, less than the differences due to the overriding puckering effect.

There is independent evidence for the suggestion that geometrical effects exist in the feldspars which supersede or take priority of any effect of Si/Al order. This is the observation of JONES and TAYLOR (forthcoming) that there are resemblances in the shape of corresponding tetrahedra not only in orthoclase and microcline with the Si:Al ratio of 3:1, but also in celsian with the 1:1 ratio.

When we turn to the question of Si/Al order, we have to remember that each crystallographically-inde-

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(1) (Note added in proof, May 1961.) I now think that the actual transition temperature may be higher than this — see later discussion.

pendent set of atoms may have a different value for the energy of Si/Al substitution, and that these values may vary with the temperature as well as with the extent of replacement of neighbouring atoms, and may even change their relative sequence. It is clear from the evidence of the plagioclases, and in particular the e-plagioclases, that perfect alternation of Si and Al is a stable and satisfactory arrangement. But this requires a 1:1 ratio. What happens to the extra Si at other compositions? There are three different possibilities, each of which may play a part: (i) random entry into some sites without disturbance of any neighbours, (ii) concentration in anti-phase boundaries which may later be organised by annealing into stacking faults, (iii) closed-circuit reversal of Si/Al sequence over small groups of atoms, so as only to give Si-O-Si in particularly favourable places. Using these it is possible to derive a continuous series from anorthite to high albite, but not to low albite.

At the albite end, where the 3:1 ratio is approached, the different ordered groupings are likely to have smaller energy differences and hence a more complicated temperature dependence. We may illustrate it as follows.

Suppose we have a completely disordered material, and plot its energy against any geometrical parameter —say an obliquity. This is shown in Fig. 2 a for one particular temperature. Actually instead of a linear curve we should have a surface of as many dimensions as there are independent geometrical parameters, but one will suffice for illustration. The minima in the curve represent equilibrium positions; the deeper the minimum the more stable the equilibrium. The shape fo the curve will be sensitive to temperature, even if disorder remains complete. At another temperature, the relative depths of the minima may be changed, as in Fig. 2 b. If there is no change in the ordering, it is easy to go reversibly from 2 a to 2 b; this would be true also for a perfect structure or a partly disordered one. But suppose the conditions are such as to allow interchange of atoms, even if slowly. The structures corresponding to the lowest minima of 2 a and 2 b are different. Consequently there may be differences in the extent to which any particular site favours Si, and annealing may bring about different patterns of ordering. In each case the deepest minimum will become deeper, perhaps changing its position continuously as it does so, as shown in Figs. 2 c
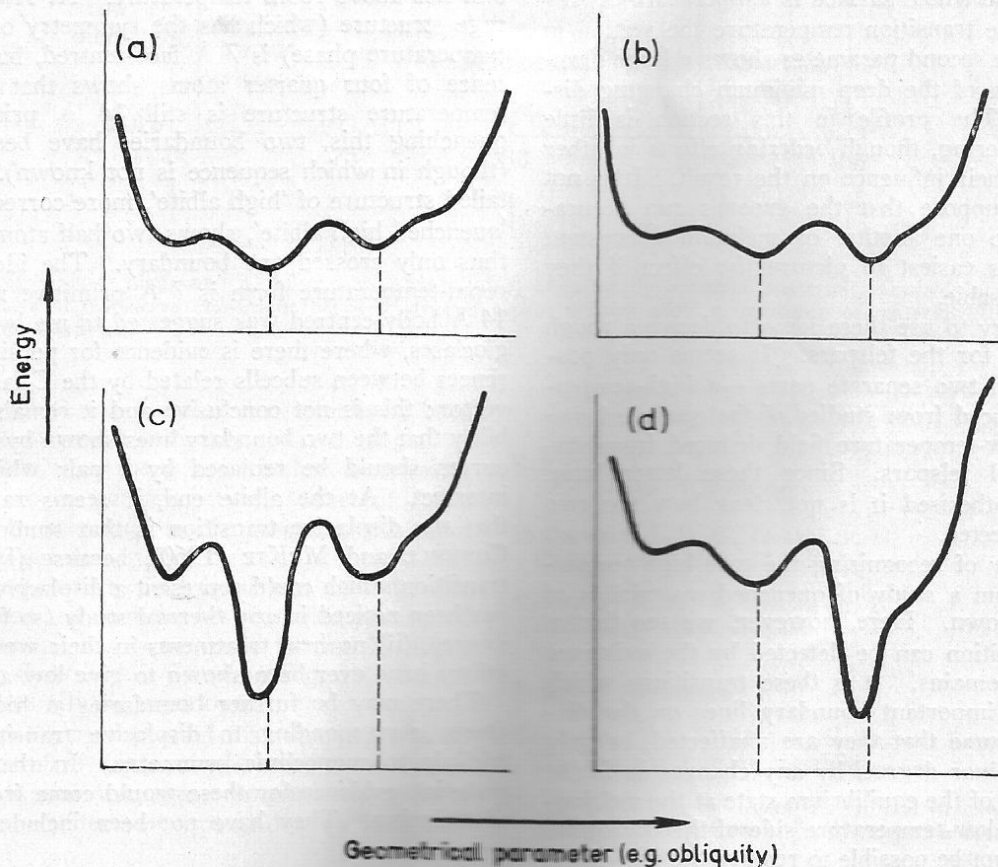

Fig. 2.—Plot of energy (ordinate) against a geometrical parameter (abscissa) for a hypothetical material; (a) and (b) represent completely disordered states at different temperatures, (c) and (d) the equilibrium ordered states obtained by annealing at the two temperatures.

and 2 d. If now material annealed at the first temperature is brought to the second temperature, the energy surface will change, but probably not so such as to destroy the minimum; the changes of parameter are more likely to be comparable with those of ordinary thermal expansion. If annealing is continued, there may be some changes in the degree of order, but in general the state of 2 b (or 2 d) can never be regained from 2 c, except *via* a temperature where the equilibrium state is one of complete disorder, because the path to it has been closed by the deepening of the different minimum in the first annealing.

This picture enables one to understand how the state of a felspar may depend on its thermal history. It does not include any account of the puckering transition, which is in some ways more fundamental. For this, we may consider a second geometrical parameter plotted at right angles to the paper, so that if the plane of Fig. 2 is put vertical the general trend of the energy surface is more or less horizontal. Suppose that the profile of Fig. 2 c or 2 d does not vary much with this new coordinate; then the grooves traverse the surface like a road with ruts in it., travelling roughly perpendicular to Fig. 2 but going up and down hill, with one deep valley representing equilibrium. But the whole surface is temperature-dependent, and at the transition temperature the section in the plane of the second parameter shows a large change, the position of the deep minimum changing discontinuously. The profile in this section is little affected by ordering, though ordering effects in other sections have their influence on the result. It is not necessary to suppose that the grooves run accuratelly parallel to one another or maintain a constant depth, but it is easiest to picture the effect if they remain recognisable.

I will now try to use these ideas to derive a rough phase diagram for the felspars. It seems only possible to do it in two separate parts —a high-temperature field deduced from studies of the quenched material and a low-temperature field deduced from studies of natural felspars. Since these latter have never been synthesised it is not clear how the two fields are connected.

The difficulty of recognising the true high-temperature phase from a study of quenched material is of course well known. Here, however, we see that a displacive transition can be detected by the existence of anti-phase domains. It is these transitions which form the most important boundary lines on the diagram. We assume that they are unaffected, or only affected to a minor degree, by any changes in Si/Al order from that of the equilibrium state at the melting-point. On the low-temperature side of the transition, it may or may not be possible to remove the anti-phase domains by annealing. Where it is not possible, the evidence for the existence of the low-symmetry form is of course more controversial. One has to assume

that in many cases diffraction broadening is sufficient to render the characteristic difference reflections completely unobservable in experimental work so far. In support of this are the observed facts in the anorthites, where we have a progressive series of intermediate cases culminating in the effective disappearance of the set of spots concerned. Further experimental work with long exposures or new techniques may reveal other examples, but large-cell structures with very small domains might still escape direct detection.

Fig. 3 a represents the quenched material. The curves are very roughly sketched; only near the anorthite end are the temperatures known. Here there is clear-cut evidence for the existence of the 14 Å primitive structure and the transition above 1200° C., and there seems no reasonable doubt of the existence of the 14 Å body-centred structure, continuing up to the melting-point over an appreciable composition range (2). The initial rapid drop of temperature with decreasing anorthite content is also experimentally established. By An_{80} only the a- and b-type reflections characteristic of a 14 Å body-centred structure remain, but detailed investigation shows that these correspond to an average structure containing two pairs of half atoms, indicating that the boundary line still lies above room temperature. At An_{50} the average structure (which has the symmetry of the high-temperature phase) is 7 Å face-centred, but the existence of four quarter atoms shows that the room-temperature structure is still 14 Å primitive. In quenching this, two boundaries have been crossed (though in which sequence is not known). The detailed structure of 'high albite', more correctly named 'quenched high albite', shows two half atoms, and has thus only crossed one boundary. The idea that the room-temperature form is 7 Å primitive rather than 14 Å body-centred was suggested to me by the e-plagioclases, where there is evidence for persistent differences between subcells related by the C-face-centring vector; this is not conclusive and it remains a possibility that the two boundary lines shown by the dashed curves should be replaced by a pair which do not intersect. At the albite end, it seems rather likely that the displacive transition is that studied by Mc-CONNELL and McKIE (1960), because (i) no other transition which could represent a displacive boundary has been noticed in any thermal study (so far as I am aware), (ii) no heat treatments in their work (or any other) have ever been shown to give low albite.

There may be further boundaries at high temperatures corresponding to displacive transitions from triclinic to monoclinic symmetry. In the quenched material, evidence for these would come from studies of twinning. They have not been included, because

(2) (Note added in proof, May 1961.) Though I now think that the actual transition temperature is well above 1200°C (see discussion below) the general argument holds good.

they represent a separate large problem not directly related to the experimental work on structures underlying this paper, and also because empirically we can always get (though sometimes with difficulty) material

ing attention to the importance of displacive transitions, and in so far as it is speculative or only roughly formulated I hope it may serve as stimulus to further investigation.
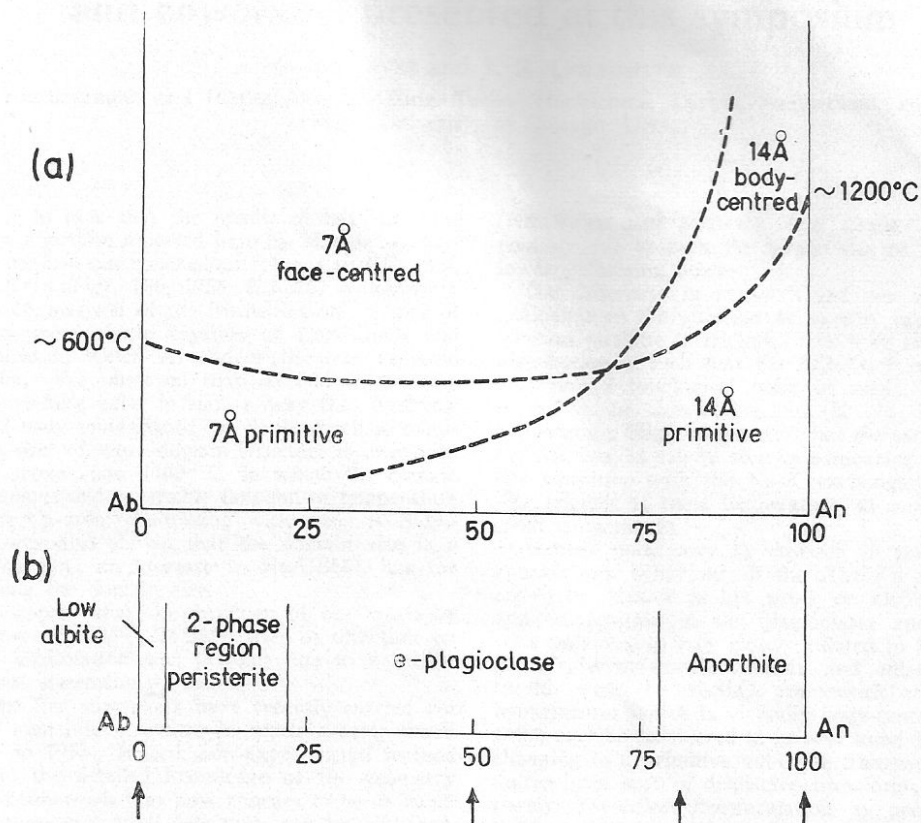
Fig. 3.—Sketch phase diagrams (a) of quenched material (b) of naturally annealed material. Dashed lines in (a) indicate boundaries of displacive transitions between structuretypes; arrows show composition of materials studied in detail at room temperature.

which is untwinned and therefore has effectively been annealed below any such boundary.

It is possible that there are further boundaries corresponding to transitions between different states of order still to be added to the diagram, but there is no evidence yet demanding it.

The low-temperature field is shown in Fig. 3 b, for completeness; it summarises commonly-accepted facts. No attempt has been made to put in upper boundaries, or show how it fits on to Fig. 3 a, because of the difficulties already mentioned.

In conclusion, it may be said that this paper is an attempt to correlate some of the results of recent structure work and use them to elucidate general principles. It provides a new point of view in direct-

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Comments on theanorthite papers by Megaw and coworkers presented at this symposium

by F. LAVES and J. R. GOLDSMITH

Institut für Kristallographie und Petrographie der Eidg. Techn. Hochschule, Zürich, Switzerland, and Department of Geology, University of Chicago, USA.

It is gratifying to note that the results of full structural determinations on anorthite reported here by MEGAW in summary form fully confirm our conclusions (*Acta Cryst.* **7**, 1954, 465-472 and *Z. Kristallogr.* **106**, 1955, 213-226) which were drawn from the comparison of the intensities and shapes of X-ray reflections from single crystals of $CaAl_2Si_2O_8$ and synthetic anorthites in which Al and/or Si were replaced by Ga and/or Ge. We observed that Al and Si are ordered up to the melting point in such a way that doubling of the *c*-axis and body-centering of the doubled cell is required, and that an «out of step»-domain structure is developed at temperatures above appr. 1100° C. in which the domain «size» is a continuous and reversible function of temperature dependent on the Ca-atom positioning within the $Al_2Si_2O_8$-framework. It was also shown that the domain size is a function of Ab-content; an increase in $NaAlSi_3O_8$ has the effect of decreasing the domain size.

It would thus appear that the criticism of our work by MEGAW (*Min. Mag.* **32**, 1959, 234-235) based at that time on her unpublished information was perhaps due to a misinterpretation of our statements.

Dr. MEGAW and her coworkers have recently carried out research on the anorthite structure in much greater detail than we had up to 1955. Indeed, our experimental method could not lead to the detailed knowledge of the geometry of the $Al_2Si_2O_8$-framework that now appears to be at hand. It is hoped that these structural data will soon be published.

There does however appear to be a difference of opinion as to the structural mechanism that produces the observed effects. In our discussion we considered only the Ca-atoms as being responsible for the fact that at temperatures below 1100° C. anorthite is primitive (with the obvious consequence that the *topologically* body-centered ordered $Al_2Si_2O_8$-framework loses its *structural* body-centering) whereas Dr. MEGAW stresses the point that the $Al_2Si_2O_8$-framework itself is responsible for the structural behaviour (with the obvious consequence that the Ca atoms also cannot be structurally ordered in a body-centred array). Actually, it would appear that both «components», the $Al_2Si_2O_8$-framework and the Ca atoms cooperate in producing the primitive symmetry. That the Ca plays a not inconsequential role is strikingly shown by the fact that $BaAl_2Si_2O_8$ *is* precisely body-centred

(NEWNHAM and MEGAW: *Acta Cryst.* **13**, 1960, 303-313), possibly due to both the larger size of the Ba ion and its lower polarizing power.

The difference in MEGAW's and our views is in a sense analogous to the question as to why sanidine is monoclinic whereas analbite is triclinic? In both structures the Al/Si-distribution is such that the $AlSi_3O_8$ framework is monoclinic from a topological point of view. Decisive roles are played by the sizes of the ions (K, Na; Ba, Ca) *and* by the temperature. High temperature has the same effect as enlarging the ions, as can be seen by comparing the analbite-monalbite transition with the Na-K exchange leading from analbite, triclinic at room temperature, to sanidine, monoclinic at room temperature.

Another point may be stressed in this connection. The «puckering» behaviour of the $Al_2Si_2O_8$ framework as described by MEGAW in her paper on «Effects of temperature and composition in the plagioclases and other feldspars» (this volume), is very closely related to BUERGER's concepts of «displacive transformation» and «distortional disorder». In this sense the $Al_2Si_2O_8$ framework of anorthite at high temperatures which is virtually body-centered at the melting point, may be considered to possess some distortional disorder changing to a primitive anorthite framework at low temperatures by a sort of displacive transformation. If it were a purely displacive transformation as proposed by MEGAW, without any control or influence induced by rearrangement of the Ca atoms (which we consider to be important), it should be expected that the high-temperature state could not be quenched in. $CaAl_2Si_2O_8$ might thus be expected to behave like $NaAlSi_3O_8$ where the monalbite-analbite-transformation cannot be suppressed either during quenching or rapid heating through the inversion temperature. But, it does not do so. The fact that we were even able to measure the «out-of-step» domain sizes qualitatively in anorthite as a function of temperature, by X-raying at room temperature, indicates the important role of the Ca atoms in the process of domain enlargement. This enlargement ultimately leads to the primitive anorthite structure at low temperatures; below 1100° C. the domains become so large that the diffuseness of the c-type subsidiary reflections, indicative of the domain development at higher temperatures, is no longer observable.

DISCUSSION

MEGAW (Cambridge):

I recognise the value of the experimental work of Professor GOLDSMITH and Professor LAVES reported in the papers quoted, and their proof of the dependence of domain size on temperature above 1100°C. I cannot, however, accept all their arguments in drawing conclusions, in particular those purporting to show that domain size is «dependent on the Ca atom positioning within the $Al_2Si_2O_8$ framework». I believe their whole concept of out-of-step domains to be different from

mine. Having assumed two equivalent sets of sites for Ca, relative to an effectively unchanged $Al_2Si_2O_8$ framework, they define domains as «volumes within the crystal in which A sites on the one hand, and B sites on the other predominate», and they state that «the energy required to shift an individual atom from an A site to a B site is very small». Against this, structural evidence shows that the Ca have specific, non-equivalent sites, closely gripped by the O atoms of the framework; with their surrounding sections of the framework they alternate perfectly within a domain, change of

step from PQPQP ... to QPQPQ ... taking place only between domains, at the boundaries. I think the present discussion confirms that there is a real difference of viewpoint, a difference which I tried to make clear in my 1959 paper.

I agree that neither the Ca atoms alone nor the $Al_2Si_2O_8$ framework alone can be thought of as «responsible for» variations in the structure. But if the energy of the structure is considered (in the usual empirical way) as built up from independent contributions associated respectively with the cation-oxygen repulsive forces, the rigidity forces of the framework, and the cation-oxygen ionic or semipolar attractive forces, we can assess their relative importance. Replacement of Ca by Ba, while keeping the framework unchanged, would alter very greatly the large contribution from the repulsive forces; it is not surprising that this outweighs the energy needed for angular distortion of the framework and makes stable a different configuration. On the other hand, the framework distortion energy is likely to be large compared with the Ca-O attractive energy. In this sense the framework is more important than the Ca atoms. It is true that Ca cannot take up a configuration which fails to provide an energetically reasonable environment for each it atom, but still less can the Ca's impose an energetically unfavourable configuration on the framework. I believe that there is a greater variety of permissible Ca environments than of framework configurations, and therefore that the balance achieved is best considered as determined essentially by the framework though modified by the large cation. The same argument will apply to other felspars also.

In my view the anorthite transition *is* a displacive transition, differing from the displacive transition described by BUERGER only in that the symmetry lost in the low-symmetry ('derivative') structure as compared with the high-symmetry ('basic') structure is a translation repeat instead of a symmetry axis or plane. Just as in BUERGER's example the derivative structure may appear with either of two orientations, in anorthite it may appear in either of two parallel positions, with different choice of origin, which we may call 'translation states'. Where the two translation states occur together they form antiphase domains, just as where two orientations of BUERGER's example occur together they form twin components. Within a domain, the structure is perfect, though there may be strain at the domain walls.

The application of these ideas to the anorthite transition explains the experimental work of LAVES and GOLDSMITH without attributing special powers to the Ca atom. As the temperature rises above 1100° C., the free energy of the body-centred phase becomes comparable with, though still greater than, that of the primitive phase. Thermal fluctuations will then bring about local transitions, and the crystal as a whole will consist of a shifting mosaic of small domains of the two translation states of the primitive structure separated by small domains of the body-centred structure. The experimental results, I now recognise, suggest that this two-phase region continues to near the melting point. The higher the temperature, the greater the proportion of material instantaneously in the body-centred phase. On quenching, this phase reverts at once to primitive, adopting the translation state of the domain adjacent to it; if it separated two domains of different translation state, an antiphase domain boundary remains to mark its place. Thus large volumes of body-centred material in the two-phase region mean large areas of domain walls on quenching, and hence, for a given volume, small domains. This explains the observed dependence of domain size on quenching temperature.

According to this view, the *texture* of a high-temperature material near a displacive transition can be quenched in — as is indeed familiar in many xamples of polysynthetic twinning — but the *structure* of the high-temperature form cannot be quenched in (unless the domains are so small that the surface energy of their walls becomes a preciable).

This implies that the structure of quenched 'high anorthite'

is the same as that of primitive anorthite. I believe that it is so. This prediction can be tested experimentally, though because of the diffuseness of the c-type reflections it will be necessary to examine a superposition of the two translation states rather than one alone. Work on the subject has been started, in collaboration with Mr. P. H. RIBBE. The prediction is that 'high anorthite' will not differ significantly from primitive anorthite.

LAVES (Zürich), reply:

1. Dr. MEGAW distinguishes between PQPQP... and QPQPQ... domains. We distinguished AAA... and BBB... domains. Whether a domain is a PQ or a QP domain (in MEGAW's definition), or if it is an A or a B domain (in our definition) depends on the choice of the origin or the signs of the system of the coordinates. (Cp. *Z. Kristallogr.* **106**, 1955, 222-225.) The only difference we can see right now is that we only could propose (1954, 1955) a schematical model (for illustrating the principle) whereas Dr. MEGAW may now be able to give a more specific picture on the basis of Cambridge work as yet unpublished, and that Dr. MEGAW puts more weight into the metrics of the Al, Si-framework, whereas we (on the basis of reflected intensities of the c-spots) considered predominantly the metrics of the Ca-positioning. Dr. MEGAW and we now agree that (to be more rigorous) both metrics should be considered.

It may be mentioned, however, that we have been aware of the fact that the metrics of the $AlSi_3O_8$-framework is not independent of the metrics of the Ca-positioning. (We considered the c-reflections as «reflections that have structure factors made up predominantly of Ca contributions»; note the word «predominantly», we did not say «only».)

2. Another point needs clarification. Dr. MEGAW states in her reply: «Against this, structural evidence shows that the Ca atoms have specific, non-equivalent sites», implying that we missed this point. However, *we did not exclude* this obvious necessity, for we were aware of the fact that a cell of primitive 14 Å-anorthite contains 8 Ca ions, i.e. there *have* to be at least four Ca lattice complexes which are not equivalent. We expressed our awareness of this by stating (A. *Cryst.* **7**, 1954, 468) «There are two euivalent sets of lattice complexes that can be occupied by calcium ions; either arrangement produces an identical anorthite structure. These two sets can be called A and B». Thus, we did *not* talk of two equivalent «sets of sites» (as Dr. MEGAW is quoting us) but of two equivalent «sets of lattice complexes». Perhaps it would have been better to use the word «indistinguishable» instead of equivalent in which case this misinterpretation by Dr. MEGAW might not have happenend. No evidence against this concept has yet been put forward by Dr. MEGAW.

3. In the first paragraph Dr. MEGAW argues against our definition of domain size. However, it is an experimental fact that the «domain size» is a function of temperature. This means: raising the temperature leads to a smaller size, i.e. new out-of-step boundaries must be formed. This may take place in the following way: Within a large A-domain a small nucleus of a B-domain may be formed (and vice versa). A preliminary stage (before a definite B-domain is formed) might be a structural fluctuation showing some tendency in the direction of a B-domain («distortional disorder» within the A-domain). To allow for such possibilities we defined our domains as «volumes within the crystal in which A sites on the one hand and B-sites on the other hand predominate». Translated into the language of Dr. MEGAW this definition would read: «Volumes within the crystal in which exact PQPQ... sequences on the one hand and exact QPQP... sequences on the other hand predominate». For example a sequence ...PQPQPQ.QP.PQPQPQ... would be in our sense a PQ domain in which the exact PQ sequence predominates.

Even if such small sequence mistakes would *not* occur (a proof might be hard to provide) our definition would not be wrong, as we did not specify the «amount» of predominance.

4. In this connection another suggestion of Dr. Megaw should be discussed. She writes in her comment: «The experimental results, I now recognize, suggest that this two-phase region continues to near the melting point. The higher the temperature, the greater the proportion of material instantaneously in the body-centered phase». This suggestion (not accompanied by any additional experimental work) comes quite near to our earlier definition of domain size: as the sizes of A and B domains become smaller the amount of boundary material will increase, because we do not believe that there is a *sharp* boundary between an *exact* A-domain and an *exact* B-domain. We believe that *at* an A-B-domain-boundary there is a more (at high temperature) or less (at low temperature) continuous change from A-orientation to B-orientation, passing through a «body-centred structure». (To avoid further discussions of a semantical character we have put the words *body-centered structure* between quotation marks because at this stage and before X-ray investigations have been carried out *at* high temperature we are disinterested in the question how thick a wall should be to be recognized as being made up by body-centered material, and how many mistakes may it be allowed to contain for said recognition; or, the other way around, we are disinterested in the question of decision, where a domain ceases to be a domain of primitive anorthite structure. — To describe the whole story rigorously, quantitatively and completely the development of a rather complex, temperature dependent, formula —based on energy and probability considerations— would be necessary). A middle (probably irregular) plane within the «body-centered wall region» divides A-domains and B-domains in which the A-state and the B-state «predominate».

5. As to the second last paragraph of Dr. Megaws comments we fully agree (see point 4 above). Certainly quenching from high temperature may not prevent but most probably enhance the perfection of the A-state and B-state within the A- and B-domains. During such quenching the «average size» of the A and B domains may even become somewhat enlarged.

6. In this connection a general remark may be permitted. We do not know much about the actual shape of the domains [except the elongation of the c-spot streaks indicates some preference of platyness parallel (010)]. Additional work is necessary to answer this question. The domains may be finite or infinite in one to three dimensions (in the extreme, they may be but two interwoven frameworks that are unlimited in all three dimensions). Thus, talking of a «size» of the domains may sound rather vague and undefined. In realizing this we have been frequently rather hesitant to use the word «size» and, therefore, we frequently preferred to stress more the increase of the amount of boundary material with increasing temperature rather than the increase of the domain size.

7. In the fourth paragraph of her answer Dr. Megaw states that she can explain our 1954 experiments «Without attributing special powers to the Ca atom». We believe any reader of our papers will realize that we did *not* attribute «special powers» to the Ca atom. What we did was to point to those consequences of our experiments which suggested that Ca ions have to move (by small amounts) when an area of A-state changes into one of B-state, and vice versa. As we realized —see the last paragraph of point 1 above— that in connection with the Ca movements the $AlSi_3O_8$— framework has to change too, Dr. Megaw's explanation of our experiments on the «anorthite-transition» does not deviate from our explanation as far as the principle is concerned. It is true, Dr. Megaw developed a more detailed (but not different) picture of the «transition»-process, however in part only describing it with *words* «different» from those we had used.

8. The problem, whether the «anorthite-transition *is* a displacive transition» (as Dr. Megaw says) or whether it is «very closely related to Buerger's concepts of displacive transformation and distortional disorder» (as we preferred to say in our comments) appears to be a matter of definition or semantics which can only be solved at this stage by deciding on the following question: Should we *call* this anorthite-«transition» a displacive one or not. If we should decide to call it a displacive transformation, the original definitions given by Buerger should be amended in several respects, especially with respect to the point of the domain— «size» being a reversible function of temperature. We believe (at least for the present time) it would be wise to *discriminate* between the concept of displacive transformation (as defined by Buerger) and the kind of transition here in question. A word like «district» transformation might not be a bad one; it would indicate its most important feature, i.e. the change of the domain (district)-size as a function of temperature. It may be admitted that later work may show that all displacive transformations in the sense of Buerger have a small temperature range just below «the transformation temperature» (or even above?) in which a twin size dependency with temperature could be observed by carefull measurements. However, if this would be so the states within such temperature range may perhaps also fit the definitions Buerger gave for his concept «distortional disorder». Thus, it may finally turn out, that a distinction between displacive and district transformation would be meaningless as far as principles are concerned, but such a distinction will certainly be convenient for practical purposes. (Whereas to the best of our knowledge anorthite was the first example in which a «district transformation» was observed, some ferroelectric materials have ben reported in recent years that show an analogous behaviour: a domain size-temperature dependency).

9. It is hoped that the critical discussions above will contribute to a better understanding of the transitions taking place in anorthite when heat-treater, and will indicate that our 1954, 1955 suggestions are in line with Dr. Megaw's liter and more detailed work but not incorrect as implied by Dr. Megaw's 1959 criticism. We consider Dr. Megaw's point of view (derived from the full structure determinations here reported on) that the puckering tendency of the Al-Si-O-frameworks in the feldspars (and in other silicates) plays an essential role as far as symmetry and transitional behaviour is concerned as a very important step in the devolopment of our knowledge of the feldspars (and silicates).

Megaw (Cambridge), comment to point 3:

Professor Laves' further explanation of his earlier work, which carries the implication that he there used the word «site» in an nusual way to mean an extensive piece of structure, has made it clear that the differences between our concepts are much less than I had originally supposed. I agree in thinking that the discussion has served a useful purpose of clarification and I am very glad of it.

I agree that I ought to have been content at the present stage to say that the transition «is very closely related to» a displacive transition rather than that it «is» a displacive transition. My conception of «displacive transition» probably involves an addition to Burger's picture, namely the assumption that with further increase in temperature the whole of the material is transformed into the more symmetrical or «open» form, so that transient domains of the less symmetrical form are no longer recognisable. This is comparable to effects in ferroelectrics and implies a transition range in which the «open» form coexists with shifting domains of the two orientations of the less symmetrical form. Buerger describes the state near the lower end of this coexistence range; in anorthite, from the evidence of Laves' results, the upper end would seem to lie above 1500° C. I would regret the introduction of new names for transition types until more is known.

Some recent work on the plagioclase feldspars

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ABSTRACT

Now that the general features of the sub-solidus relationships of the plagioclases have been established by X-ray studies, more detailed work is being undertaken. Two aspects of this work are referred to in the present paper.

Firstly it is necessary to elucidate more carefully the nature of the various phase changes which can take place. Whilst the detailed analyses of the atomic structures of the various phases are invaluable to a complete understanding of the transformations, other evidence can be obtained by a study of the dynamics of the transformation process. A review of some of the methods employed and the results which they have yielded are given in the first part of this paper.

Previous work has clearly established that the structural state of a plagioclase can be determined both by optical and X-ray methods. A combined optical and X-ray study of the plagioclases of the Skaergaard intrusion, E. Greenland, has been made both to correlate the results of optical and X-ray determinations and to see if a detailed study of the feldspars could be of use in the interpretation of the cooling history of the complex. An account of the results of this study are given in the second half of this paper.

In the last decade, it has become apparent that the plagioclase feldspars have complex sub-solidus relationships. The general features of these relationships have now been established, and now various kinds of more detailed study must be carried out. Fundamentally it is a problem of defining the fields of the various phases, their stability relationships and the nature of the structural re-organisations which occur with the transformation of one phase to another; only when this has been completely done will it be possible fully to assess the usefulness of the plagioclases in petrological interpretation. In this contribution I shall outline two aspects of this work which are being investigated at the Department of Mineralogy and Petrology, Cambridge; I shall make specific references to my colleagues who are engaged on this work at the appropriate places in the paper.

We have heard about the detailed analyses of the atomic arrangements of the various structural modifications being carried out in the Cavendish Laboratory under Dr. Taylor's direction; these will undoubtedly prove invaluable for the complete understanding of the various phase changes that take place. However, much useful information can be obtained by a study of the dynamics of the transformation process, and it is with this approach that I want to concern myself in the first half of this paper.

THE STUDY OF EQUILIBRATION RATES

a) *Methods.*

The kinetics of chemical reactions have been extensively studied by physical chemists. The simpler ideas of reaction kinetics have been used in the present work on the plagioclases, for there are many parallels between the transformations and ordinary chemical reactions. Principally, we shall use the fact that at a given temperature and pressure the transformation rate varies with time, so that from a study of the rate of approach to equilibrium under different physical conditions it is possible to obtain constants characteristic of the transformation at each temperature and pressure etc.

Formally the kinetic analysis follows closely that adopted for ordinary chemical reactions. The rate of approach to equilibrium is likely to be dependent in a simple manner on the departure from equilibrium at that time. Thus if we take some quantity ψ as a physical measure of the transformation, it will be probable that the rate law for the transformation will fit the simple form.

$$- d\psi/dt = k (\psi - \psi\infty)^n$$

ψ_{oo} is the value to which the quantity ψ tends at infinite time i.e. when the system is completely equilibrated, k is the rate constant which is fixed for given physical conditions, n defines the order of the rate law. In ordinary chemical reactions, n is 1, 2 3, etc., for first, second, third order reactions depending on the number of molecules involved. In our case the order of the reaction will be defined by the precise mechanism of the transformation which is not known. This is not important, however, as the rate law can be empirically determined for particular physical conditions by observations of the change in ψ with time; the significance of the order of the rate law need not concern us. As an example of procedure, it was found that a second-order rate law controlled the high-low albite inversion, for the data fit the expression

$$kt = (\psi_o - \psi)/(\psi - \psi\infty) \ (\psi_o - \psi\infty)$$

derived by integrating the rate law for $n = 2$ and inserting the limit $\psi \to \psi_0$ as $t \to 0$. Fig. 1 shows the variation of $\log (\psi_0 - \psi)/(\psi - \psi_\infty)$ vs. $\log t$ for synthetic $NaSi_3AlO_8$ treated hydrothermally at $700°$ C., $p_{H_2O} = 28000$ lb/in². [The character of the parameter ψ used in this case will be discussed later].

character of the transformation. In solid state transformations, those that show classical discontinuity in, for example, measured specific heat and molar volume as a function of pressure and temperature, can be distinguished from continuous transformations that show no such discontinuity. UBBELOHDE (1957)
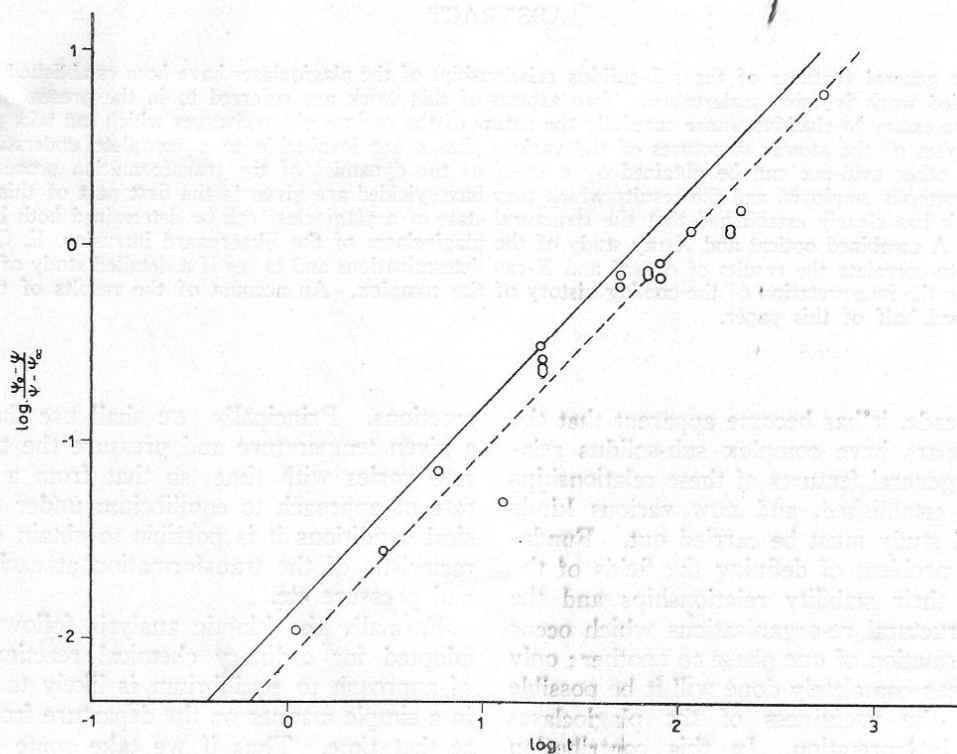
Fig. 1.—Logarithmic plot of $(\psi_0 - \psi)/(\psi - \psi_\infty) = kt (\psi_0 - \psi_\infty)$ for $700°$ C., $p_{H_2O} = 28000$ lb/in².

From this plot, the value of the rate constant, k, can be derived for these experimental conditions.

Having derived the different rate constants for various physical conditions, the temperature dependence of the rate processes is described by the Arrhenius relationship

$$k = Ae^{-\frac{E_a}{RT}}$$

where k is the rate constant at absolute temperature T, E_a, the activation energy for the rate controlling mechanism, R, the gas constant, A, commonly called the frequency factor, is a term including the entropy of activation. Within the temperature range of a transformation, A may change in value owing to a change in the mechanism of the diffusion process; outside such a temperature range A should be relatively independent of temperature. By plotting $\ln k$ vs. $1/T$ we should get a linear plot, from which the activation energy E_a can be found. Furthermore the nature of this plot can give information about the

has applied the term "smeared transformation" to transformations where continuity can be associated with the stable co-existence of two or more closely related structural modifications over a range of temperature. The Arrhenius plots may therefore provide direct evidence on the character of the transformation (Fig. 2).

b) Experimental Results.

Similar methods for the derivation of rate constants have been used by other workers employing measurements of electrical conductivity and diffusion coefficients for the physical parameter ψ (see UBBELOHDE). McKIE (1959), in a study of the high-low transformation of yoderite, an alumino-silicate, first applied the treatment to X-ray data; in this work, he used the fading in intensity of certain subsidiary X-ray reflexions as a measure of the rate of transformation. Later McCONNELL, and McKIE (1960) started the present work on the feldspars with a kinetic analysis
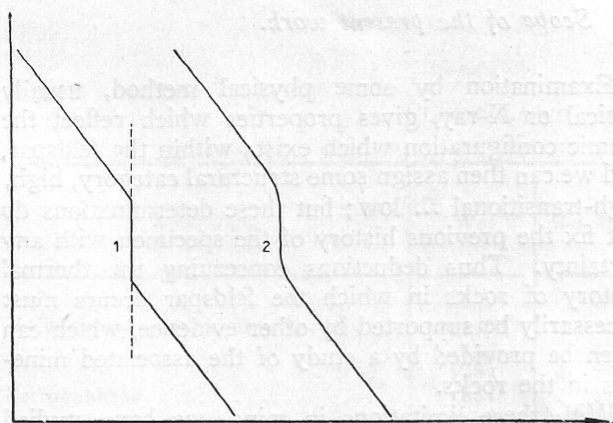
Fig. 2. – Hypothetical Arrhenius plots of discontinuous (1) and continuous (2) transformations.

of the data of MacKenzie (1957) on the hydrothermal treatment of $NaAlSi_3O_8$ under isobaric, isothermal conditions. Here again X-ray data provided the physical parameter, but this time the variable separation of two lines on the diffractometer trace was used as a measure of ψ. Since then there has been further experimental work done with a view to obtaining similar analyses of other transformations in the plagioclases, but the amassing of the data is tedious and often difficult, so that I am able only to give a progress report on this work. Firstly
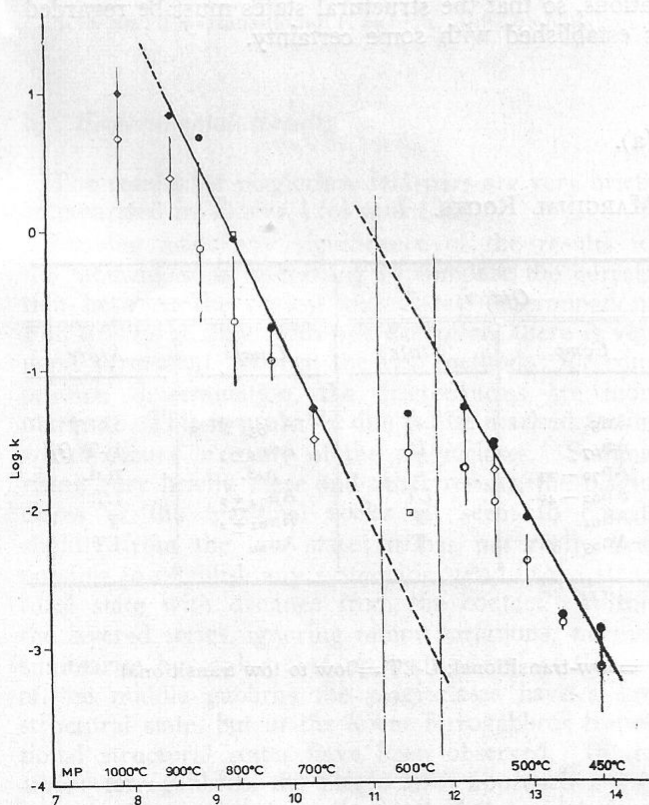
Fig. 3.—Plot of logk vs. T^{-1}.

The hydrothermal treatment of $NaSi_3AlO_8$: McConnell and McKie (1960) found evidence from MacKenzie's data (1957) for a smeared thermal transformation of considerable magnitude probably in the range between 575° C. and 625° C. for P_{H_2O} 14000 lb/in² (Fig 3). The activation energy for the transformation was determined as 60 kcal./mole. The discontinuous or smeared transformation at about 600° C. implies that there is a rapid change in the degree of order of Al and Si, with slower changes above and below the critical region. The activation energy for the transformation is compatible with a rate-controlling diffusion mechanism involving Al-Si order in the structure. The Si-O bond energy has been previously estimated as of the order of 90 kcal./mole. This does not imply, however, that the rôle of the sodium atoms in controlling the transformation can be discounted.

Dry heating of $NaSi_3AlO_8$: From some data on dry heating obtained by MacKenzie, it was found that there is a profound difference between the equilibration rates for dry and hydrothermal transformations, being 200-2000 times slower under dry conditions. It seems probable that this must be directly associated with the direct participation of water or its dissociation products in the transformation mechanism. McConnell and McKie have begun to investigate this further by obtaining more data for dry heating.

Dry heating of intermediate plagioclases: We thought that the rate constants could be best determined by measuring the rate of disappearance of the subsidary type (e) reflections in the manner that had previously been done for yoderite. A specimen from the Stillwater complex, An_{63}, has been used for this difficult work. To date, a satisfactory rate curve has been obtained at one temperature (1050° C.) by Bown, but results at other temperatures have not been consistent.

Dry heating of anorthites: We have also looked into the possibility of investigating the rapid, reversible transformation primitive → transitional → body-centred anorthite in this manner. As a measure of the transformation, both the rate of disappearance of the $(11\bar{1})$ reflexion, and the change in the B angle of Smith and Gay (1958) have been used. In both cases, limitations of experimental accuracy have so far prevented any rate curve from being determined.

c) Petrological Considerations.

Clearly at the present stage of the work the petrological applications are very restricted. The implications of their work on the albites have been summa-

rised by McConnell and McKie, but they add very little to what we have already known about the occurrence of low and high albites. Nevertheless fuller studies are likely to yield much more specific information which will ultimately be of value in petrological interpretation.

In the second half of this contribution I want to discuss a different topic with which Dr. I. D. Muir, as well as some of my other colleagues already mentioned, has been concerned.

THE FELDSPARS OF THE SKAERGAARD INTRUSION

So far as we know, modern techniques have not been applied to the detailed study of the feldspars of an igneous complex. We have examined the structural states of plagioclase feldspars throughout a single intrusion, and have attempted to relate these, where possible, to any other thermal data available from studies of associated minerals. In this way, we can find out how much light is thrown by such an investigation on any interpretation of the cooling history of the complex. The well known Skaergaard intrusion is ideally suited for this type of work, for the careful and detailed study of Wager and Deer (1939) together with the work of later authors, has resulted in its petrology being better known than that of any other complex. We are indebted to Professors Wager and Deer for their kindness in providing specimens.

a) *Scope of the present work.*

Examination by some physical method, usually optical or X-ray, gives properties which reflect the atomic configuration which exists within the feldspar, and we can then assign some structural category, high, high-transitional ... low; but these determinations do not fix the previous history of the specimen with any certainty. Thus deductions concerning the thermal history of rocks in which the feldspar occurs must necessarily be supported by other evidence, which can often be provided by a study of the associated minerals in the rocks.

With these limitations in mind, we have studied the feldspars, mainly plagioclase, from about 30 rocks selected as typical of the chilled margin, the marginal border group and the laminated and unlaminated layered series of the intrusion. The feldspars from each rock have been examined by optical and X-ray methods. Thin sections cut from each specimen were studied by universal-stage methods, whilst the X-ray examination has been carried out mainly on selected single crystals typical of the feldspar of the selected rock. The optical and X-ray examinations can be regarded as complementary, each yielding independent data to correlate and combine to give a reliable assessment of the structural state of the particular feldspar. Our results show that there is an excellent correlation between the optical and X-ray determinations, so that the structural states must be regarded as established with some certainty.

Table 1 (a).

Plagioclases of the Marginal Rocks.

Rock Type	No.	Location	Optics		X-ray	
			Comp.	State	Comp.	State
Marginal Border Group........	1837	30 m. from contact	An_{63}	L-T	An_{63}	L-LT
	4500		An_{67}	L	$An_{65 \pm 3}$	L-T (?)
Perpendicular Feldspar Rock ..	1849		An_{70-73}	L	n.d.	n.d.
Chilled Margin	4507	25 m. from contact	An_{62-46}	LT	$An_{72 \pm 2}$	LT
	1724	25 m. from contact	An_{61}	T	$An_{61 \pm 2}$	T
	1825	3 m. from contact	An_{65}	T	An_{62}	LT

Classification of Structural State.

L = low; T = transitional; H = high, with combinations e.g.; LT = low-transitional; L-LT = low to low transitional.

Table 1 (b).

PLAGIOCLASES FROM THE LAYERED SERIES.

Rock Type	No.	Height (in m.)	Optics		X-ray	
			Comp.	State	Comp.	State
Unlaminated Layered Series.........	4136	2750	An_{44}	L-T	An_{33} (?)	T (?)
	4139	2600	An_{32}	L-LT	—	TH
Ferrogabbros	1883	2500	An_{27}	TH	—	TH-H
	1881	2450	An_{27}	H	—	H
	4142	2450	An_{32}	TH	—	H
	1713	2450	An_{31}	LT	An_{37}	L
	4143	2400	An_{32}	T	—	TH
	1974	2375	An_{34}	LT	$An_{37 \pm 4}$	LT
	4144	2300	An_{35}	TH	—	H
	4145	2200	An_{38}	TH	—	H
	4146	2100	An_{35}	TH	—	H
	4147	2050	An_{38}	T	An_{40}	T
	4272	2000	An_{37}	LT	$An_{37 \pm 2}$	L-LT
	1907	1800	An_{40}	T	$An_{37 \pm 2}$	T
	2580	1700	An_{41}	LT	$An_{44 \pm 2}$	LT
Middle Gabbros...................	3655	1500	An_{44}	L-LT	$An_{47 \pm 2}$	L
	3661	1200	An_{46}	L	$An_{46 \pm 2}$	L
	1691	1050	An_{52}	L	$An_{52 \pm 2}$	L
Hypersthene-Olivine Gabbros........	2307	850	An_{53}	L	$An_{56 \pm 2}$	L
	4077	500	An_{55}	L	n.d.	n.d.
	4084	350	An_{65}	L	$An_{68 \pm 2}$	L
Transitional Layered Series	4087	0	An_{68}	L	$An_{67 \pm 2}$	L

Classification of Structural State.

L = low; T = transitional; H = high, with combinations e.g.; LT = low-transitional; L-LT = low to low transitional.

b) *Experimental Results.*

The results for plagioclase feldspars are very briefly summarised in Tables 1 (a) and 1 (b).

Leaving aside any significance of the results for the moment, it is interesting to compare the correlation between the optical and X-ray determinations. For structural state, with one exception, there is very good agreement between the two methods; for composition determination, the discrepancies are more marked. This is probably due to the marked zoning which occurs in many of the plagioclases. Summarising very briefly these and other results, the plagioclases of the marginal rocks all seem to deviate slightly from the low state; it has not really been possible to establish any systematic trend in the structural state with distance from the contact. Within the layered series, ignoring minor variations, we may summarise by saying that up to the level of the top of the middle gabbros the plagioclases have a low structural state, but in the lower ferrogabbros transitional structural states have been observed. In the upper ferrogabbros, the plagioclases approach a high structural state; at about the level of the purple band at the top of the laminated layered series, a change

towards low states is encountered locally. From the unlaminated layered rocks, the plagioclases are in transitional states, whilst we have also found similar states in both the sodic plagioclases and alkali-feldspars, of the still later formed granophyres.

c) *Associated Minerals.*

In this intrusion a magnificent range of pyroxenes is found, which have been extensively studied in detail (MUIR, 1951; BROWN, 1957; BOWN and GAY, 1960). We have made additional observations relevant to the present work. Other associated minerals which can be valuable in the present study are the iron ores and the silica minerals. We shall not comment further on these minerals here save to say that all these observations help in the interpretation of the significance of the structural states of the feldspars.

d) *Cooling Hypothesis for the Intrusion.*

There is not the time here to discuss how all the

lines of evidence may be fitted in an attempt to obtain a coherent picture. I will attempt only to summarise the present position.

In the chilled margin most of the feldspars deviate slightly but significantly from the low state. If the intrusion is pictured as being injected quickly into the surrounding mass of cold rock, whereas the extreme margin would be chilled rapidly initially, there would soon be established a temperature gradient in the margin rising towards the inner contact with the still molten magma. Thus although we may expect to find deviations from the low state in feldspars near the outer contact, these deviations should become smaller with increasing distance from the country rock. On the whole, the experimental evidence tends to support this.

By the time the lowest exposed rocks of the layered series were formed, a vigorous convective circulation had been established in the magma chamber due to the predominant loss of heat through the roof (WAGER and DEER, 1939); this would prevent the development of any considerable temperature gradient in the liquid. In this way fresh supplies of hot liquid would be kept in contact with the newly crystallised rocks, and the temperature gradient in these, once established, should be maintained for a considerable time with the temperature at any one point decreasing very slowly. Thus in the lower part of the layered series we find feldspars in the low structural state (and regular exsolution in the pyroxene). When the lowest ferrogabbros were forming, the temperature of the remaining magma would be slightly lower than it was initially and only 10-15 % of the original liquid would remain. It is about at this stage in the intrusion that the plagioclase begins to deviate from the low state; also in this region there are changes in the exsolution textures of ore minerals and pyroxenes. All the gradual changes in the mineralogy suggest that it is the rate of cooling of the magma through a critical temperature range which was responsible for the plagioclase not being able to invert completely.

At about the level of the purple band, there seems to have been a breakdown in the convective circulation in the remaining magma chamber, together with an increase of the volatile content of the magma. The plagioclases of the rocks examined at this stage fall into two categories, a group which are effectively high, and a group which deviate only slightly from the low state. It seems possible that the explanation of these two groups is related to their position within the remaining magma chamber. It is difficult to assess the precise dimensions of the magma chamber at this stage but it would seem that specimens within the high group have probably come from the margin, whereas those in the low group seem to have been nearer the centre of the magma pool. It could then be suggested that those nearer the margin would cool more rapidly through the critical temperature range,

whereas the increased volatile content and the slower cooling near the centre of the magma might account for the low structural state of the second group of specimens.

In the latest stages, represented by intermediate and acid granophyres injected into the still hot rocks of the intrusion, both sodic plagioclases and alkali feldspars are common. The plagioclases are in a low structural state in nearly all cases. The alkali feldspars are unmixed into an effectively peristeritic plagioclase and a potash-feldspar component; the latter is triclinic with an obliquity varying from almost zero in the intermediate granophyre to maximum microcline in the acid granophyre.

e) *Conclusions.*

In the short space available to us here, it has only been possible to develop one aspect of this work; we have omitted all the detailed supplementary and inter-related evidence which can be obtained from studies of minerals other than feldspars. Nevertheless it is clear that even with our very imperfect knowledge of the plagioclases, we can confirm and extend the ideas of the cooling history of the Skaergaard Intrusion first put forward by WAGER and DEER (1939). We believe that detailed studies such as the present could be applied with profit to other similar problems, provided that the rocks containing the feldspars had also been as carefully examined as those of the Skaergaard Intrusion.

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DISCUSSION

LAVES (Zürich):

As Prof. SMITH mentioned before (a written remark of this was not handed to the chairman, however) it is interesting that McCONNELL and McKIE's results of the thermodynamical considerations with respect to the albite (high-low) transformation rates as represented in GAY's paper by fig. 3 could be correlated rather nicely to the model of structural Al/Si-distribution changes proposed by me. (Z. Krist. 113, 1960, p. 280, fig. 7).

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by HELEN D. MEGAW

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11. FERGUSON, R. B., TRAILL, R. J., & TAYLOR, W. H. (1958). *Acta Cryst.* 11, 331.
    The crystal structures of low-temperature and high-temperature albites.

12. NEWNHAM, R. E., & MEGAW, H. D. (1960). *Acta Cryst.* 13, 303.
    The crystal structure of celsian (barium felspar).

13. CLARK, J. R., & APPLEMAN, D. E. (1960). *Science,* 132, 1837.
    Crystal structure refinement of reedmergnerite, the boron analog of albite.

14. JONES, J. B., & TAYLOR, W. H. (1961). *Acta Cryst.* 14, 443.
    The structure of orthoclase.

15. KEMPSTER, C. J. E., MEGAW, H. D., and RADOSLOVICH, E. W. (In preparation, 1961).
    The structure of anorthite.

16. CHANDRASEKHAR, S., FLEET, S. G., & MEGAW, H. D. (In preparation, 1961).
    The structure of an 'absent-c' bytownite ('body-centred anorthite').

Proceedings of the International Mineralogical Association
Second General Business Meeting of Delegates

Copenhagen, August 22nd and 24th., 1960.

CONTENT

FIRST SESSION

The first Session of the General Business Meeting of Delegates of the different Member Societies of the Association was held in Copenhagen on August 22nd., 1960. 36 Voting delegates and about 100 mineralogists were present representing all the Member Societies of the Association (*).

After the calling of the Delegates by the President, the session proceeded according to the agenda.

Opening.

The President, Prof. Parker, presented the following:

«REPORT ON THE PRESENT STATE OF THE I. M. A.»

It is not proposed to devote the present report to specific happenings of the past year as these are dealt with in the reports of the Secretary and Treasurer, but rather to certain matters of principle which have called for our attention and which by their nature seem likely to be topics that will figure also on the agenda of the newly-elected Council.

I. *Composition of the I. M. A.*—In Madrid the I. M. A. was conceived as a free Association of National Mineralogical and similar Societies and this we believe to have been a most happy decision. We hope that this composition will continue to be a characteristic feature of the I. M. A. We must, however, express the belief that the active participation in the affairs of the Association of the Member Societies as such (in contra-distinction to that of the delegates as individuals) should be more pronounced than hitherto. Discussions on matters of I. M. A. policy, etc., held at internal meetings of the various Member Societies and motions respecting policy, status, etc., tabled in the name of a Member Society and not of individual delegates should be encouraged as much as possible. Any increase in the number of such motions would be a welcome sign of increasing general interest in the activities of the I. M. A. Certain suggestions for thus stimulating the participation of Member Societies and for increasing their responsibility for the functioning of the I. M. A. will be made presently.

II. *Constitution of the I. M. A.*—The original constitution as drafted and approved at Madrid was in some respects

inadequate and required the revision accorded it at the Zürich meeting. Though the revised constitution was formulated with much care and after detailed discussion it is likely that certain improvements in wording and substance can still be effected. Thus, to give an example, it would seem that the rules of procedure for nominating Candidates for election to the Council might well be stated more sharply than is the case at present and formulated in the Bye-Laws. The only rule in this connexion laid down in the present Statutes states that

«Persons occupying ... post (in the Council) must be Members of a Member Society.

There shall not be more that one Member of the Council from any Member Society, nor shall any one person hold two offices simultaneously».

Further guiding principles are left entirely to the discretion of those in office. In the present instance the following directives were suggested by the President:

(i) It is desirable to retain in the Council Members who by their activity and knowledge of the affairs of the Association are particularly capable of carrying on its business.

(ii) It is desirable (with the restriction just mentioned) to allow as many Member Societies as possible to participate in the conduct of the affairs of the Association. As the number of offices is very limited this principle involves asking several present members to the Council to make way for colleagues from other countries.

These principles have, however, not met with general acceptance and it has been urged that the interests of the Association would be better served by appointing new men to all offices. The rule restricting to one the participation of members of any given Member Society has considerably added to the difficulties experienced in setting up a suitable list of candidates for presentation to the Delegates at the Business Meeting and may call for revision. In any case we feel that those in office should be provided with more adequate guidance on the desirable mode of procedure.

A notable innovation in the revised Constitution is the method of assesing the dues of Member Societies. It is as yet too early to judge whether the modified system will prove satisfactory, but the matter should, we think, be kept under review with the object of ascertaining whether the scheme adopted is in effect beneficial to the Association.

(*) With the exception of Bulgaria.

III. *Activities of the I. M. A.*—The activities of the Association as provided for by the Constitution, namely the maintenance of Commissions to deal with certain organizational and scientific aspects of mineralogical practice and the holding of Symposia on various mineralogical themes are, we believe, proving entirely satisfactory and have already provided excellent results. The reports that have come in from the Chairmen of Commissions are most encouraging and indicate that real headway has been made toward the resolution of numerous problems affecting the day-to-day work of mineralogists the worldover. Care, must, however, be taken to prevent overlapping in the terms of reference of the individuals Commissions. Steps have been taken to correct some existing instances of this kind and others may well be necessary in future also. Motions to create new Commissions to deal with petrographical matters and the teaching of mineralogy have our full support and we think that yet others lying within the scope of the I. M. A. may usefully be created in the future and will through the channel of international discussion bring clarification where it is needed. A commission on Meteorites has been suggested and would be a case in point.

The symposia hitherto held have been very satisfactorily supported and the Volume lately published in Madrid containing the proceedings of the Zürich Meeting which is the first printed publication of the Association testifies to the wide variety of topics treated at the 1959 meeting. In this connexion the opinion may be recorded that the I. M. A. Symposia seem particularly appropriate occasions for discussing controversial matters, the treatment of which before an international audience may do much to promote understanding and clear up misconceptions. The Symposia on Twinning (1959) and Feldspars (1960) are good examples of this kind and show that the impact of different opinions may be quite as important and interesting as the communication of specifically new material. Speakers in the discussions should always be asked to give summaries of their remarks for publication.

For the satisfactory future functioning of the Commissions as also for obtaining the desired speakers in Symposia, questions of finance are likely to play an increasingly important role.

IV. *General Meetings of the I. M. A.*—We believe that the individuality of the Association can best be maintained by holding its meetings apart from those of other bodies. Independent meetings enable delegates to devote their attention solely to I. M. A. affairs beside facilitating the so necessary intercourse of the delegates among themselves. Unfortunately practical reasons of time and expense and the overburdened schedule of International Congresses make it essential for some degree of mutual adjustment of the times and places of congresses to be arrived at. In our opinion such adjustments should aim at reaching a reasonable distribution of congresses rather than their concentration at the same times and places. The 1960 meeting of the I. M. A. has (in spite of the misgivings of a minority) been timed to coincide with the International Geological Congress. For reasons beyond our control our programme has had to be concentrated into 4 days which accordingly are so filled as to leave no time for Delegates to attend the sessions arranged by the Congress for those same days. This to a certain extent makes illusory the supposed advantages of holding the two meetings simultaneously. Further drawbacks of large congresses are the problems of accomodation, etc., that inevitably arise.

A convenient distribution of congresses would be much easier to achieve if the chief International Bodies dealing with the earth and crystal-physical and -chemical sciences could come to an agreement regarding the scope of their respective activities. It is suggested that the I. M. A. should strive to arrange a meeting of representatives of the various International Bodies at which efforts would be made by mutual concessions to reach a measure of agreement in

this matter. The I. M. A. would endeavour to obtain for itself the monopoly of certain subjects that are by tradition assigned to Mineralogy and Petrology. A rota of Congresses could then be worked out, the choice between the one and the other of which would be made easier for scientists by the fact that any specified field of interest would, at least in the main, figure on only one of the programmes.

Experience gained in connexion with the Madrid, Zürich and Copenhagen meetings shows clearly the advantage of having a responsible member of the Council on the spot who is able to promote the interests of the Association by making full use of local interests and amenities. Steps to make these considerations effective are suggested in paragraph VI.

V. *Finances of the I. M. A.*—The fundamental fact to be faced in connexion with the finances of the Association is that the membership dues are the only ordinary source of income available at present and that these are hardly sufficient to pay all those working for the I. M. A. their day-to-day (office) expenses which by common consent have priority over all other forms of expenditure such as travel expenses, etc. In view of this it is most gratifying to note that the Committee and Commission meetings hitherto held have been satisfactorily attended even when held apart from a General Meeting (as was the case for the Council meeting in Zürich in January 1959 and for the meeting of the Abstracts Commission in Paris in February 1960). It is also to be noted that but few discussions and differences of opinion about financial matters have arisen. The fact remains, however, that there is a limit to the demands for the self-financing of journeys that can be imposed on the Officers, Councilors, Commission Executives, and invited Speakers and it is feared that if steps to facilitate their attendance at meetings are not taken such attendances will inevitably decline. In principle the revised statutes envisage the payment of travelling expenses. In practice funds have hitherto been lacking to provide help equitably and on an adequate scale. While the opinion has been expressed that those desiring to attend a meeting in one of the official capacities mentioned above will generally be able to obtain financial help from outside sources, e.g., their National Organization (National Research Council, National Mineralogical Society, etc.) an entirely opposite view has also been voiced. The latter stresses the fact that applicants who are not delegates of a Member Society (and this applies to a majority of the Officers, Commission Executives and invited Speakers) will find it hard to induce their National Organization to meet expenses which are incurred in the service of the I. M. A. and which by rights should be born by the I. M. A. itself. Remedies for this state of affairs which (in contrast to those involving outside help) lie in the hands of the Association itself include the following:

(i)   The adoption of a notable increase in the value of the suscription unit.
(ii)   The restriction in number of General Meetings so that the surpluses from subscriptions over a number of years could accumulate and be used at least partly to defray expenses.

Of these possibilities the first should, in our opinion, be rejected. To be really effective the increase in subscriptions dues would have to be on so large a scale as probably to be prohibitive at least for the smaller Member Societies. Because it must certainly remain our aim to attract and retain as wide and comprehensive a membership as possible, subscriptions must be kept reasonably low and any increases made in the value of the unit remain small. On the other hand, the second possibility should, we think, be carefully considered and meetings should be planned to take place at

intervals long enough to allow a certain accumulation of funds but not so long as to lead to a loosening of the ties formed at each meeting and to a drifting apart of the Member Societies. All things considered it seems possible that a three-year period between meetings might be the most generally satisfactory. Such a period would lead to the I. M. A. meetings coinciding periodically but not regularly with those of other bodies the meeting of which are based on a two or four-year rhythm. Even with this rather wide spacing of meetings it would be necessary to economise in travel expenses as much as possible.

VI. *Future development of the I. M. A.*—Though the future development of our Association will be a matter for the attention of the newly-elected Council, it will, we believe, be in order to pass on for its consideration certain premises for the satisfactory future working of our Association:

(1)   The National Societies composing the I. M. A. should participate as actively as possible in the conduct of its affairs.

(2)   The I. M. A. can only fulfil its functions if it holds rather frequent meetings and symposia.

(3)   Such meetings should have as wide a geographical distribution as possible.

(4)   General Meetings should be held at the invitation of a Member Society and under its direct auspices and organization.

(5)   No general Meeting can properly be held at which the Members of the Executive Committee (President, Secretary, Treasurer) and the Commission Executives are not present. (There will, of course, be exceptions for health and personal reasons.)

(6)   It would be wholly undemocratic to elect as Officers, etc., persons of whom it is taken for granted that they will be able to pay their own expenses for travelling to and staying at the places where the meetings are held.

The President made also some remarks on the procedure of the Sessions. After this, the following Report of the Secretary was taken as read.

REPORT OF THE SECRETARY.

The rapid development of the Association in 1958-59 made apparent the need for a General Meeting of Delegates. Such a meeting was held in Zürich from August 29th. to September 7th. 1959.

The Zürich Business Meeting.

Very important for the progress of the Association was the Zürich Meeting. Delegates from the following Mineralogical Societies assembled:

Union Minéralogique Belge (Belgium).
The Mineralogical Society of Canada (Canada).
Dansk Geologisk Forening (Denmark).
Koninklijk Nederlands Geologisk Mijnbouwkundig Genootschap (The Netherlands).
Deutsche Mineralogische Gesellschaft (Germany).
Società Mineralogica Italiana (Italy).
Grupo de Mineralogía —- Real Sociedad Española de Historia Natural y Sociedad Española de Ciencias del Suelo (Spain).
The Mineralogical Society of America (U. S. A.).
Mineralogical Society of Japan (Japan).
Norsk Geologisk Forening (Norway).
Bulgarian Geological Society (Bulgaria).

Société Française de Minéralogie et de Cristallographie (France).
The Mineralogical Society of Finland (Finland).
Osterreichische Mineralogische Gesellschaft (Austria).
Ceskoslovenska Společnost pro Mineralogii a Geologii (Czechoslovakia).
All-Union Mineralogical Society (U. S. S. R.).
The Mineralogical Society of London (Great Britain).
Schweiz. Mineralogische und Petrographische Gesellschaft (Switzerland).
Geologiska Föreningen (Sweden).

and the Meeting was attended by more than 100 active members.

Among other things, a revised Constitution was adopted and the four Commissions (Abstracts, Mineral Data, New Minerals and Mineral Names and Museums) reported to the Assembly of Delegates.

A full report of the minutes of the Business Meeting as well as the new Constitution were published in «Cursillos y Conferencias» of the Instituto Lucas Mallada. Madrid. Spain (7º (1960) 101-106).

Symposia on Twinning and Alpine Fissure Minerals.

Two Symposia were held at this meeting: One on «Twinning» where M. J. Buerger, H. Curien, J. D. H. Donnay and H. Curien, P. Hartman, W. T. Holser, I. Kostov, A. von Neuhaus, and I. Sunagawa presented papers; the other on «Alpine Fissure Minerals» where G. Fagnani, D. P. Grigoriev, M. A. Kaschkai, J. Lietz and M. R. Hänisch, Robert L. Parker, and T. von Schadlun presented papers. Prof. M. J. Buerger was Chairman of the Symposium on «Twinning» and Prof. H. E. Wenk of the Symposium on «Alpine Fissure Minerals».

Excursions.

Two field excursions were also held with about 25 participants in each. The East excursion was lead by Burri, de Quervain, Wenk and Weibel and the West excursion was lead by Niggli, Nowacki, Hügi and Styger.

New Members.

The Executive Committee of the I. M. A. accepted the membership of the following Mineralogical Associations:

Mineralogical Society of New Zealand.
The Geological Society of Egypt.
Mineralogical Society of India.

Commissions.

The following persons were added to the different Commissions:

1.   *Abstracts.*
Mrs. J. Mincheva-Stefanova (Bulgaria).
Dr. R. Van Tassel (Belgium).
Prof. I. Oftedal (Norway).
Dr. W. A. Watters (New Zealand).

2.   *Mineral Data.*
Mrs. V. V. Breskovska (Bulgaria).
Prof. M. E. Denaeyer (Belgium).
Prof. I. Oftedal (Norway).
Prof. D. S. Coombs (New Zealand).

3. *New Minerals and Mineral Names.*
   Prof. Ivan Kostov (Bulgaria).
   Prof. J. Thoreau (Belgium).
   Dr. Henrich Neumann (Norway).
   Prof. D. S. Coombs (New Zealand).

4. *Museums.*
   Prof. Ivan Kostov (Bulgaria).
   Ing. A. Hubaux (Belgium).
   Dr. Henrich Neumann (Norway).
   Dr. J. J. Reed (New Zealand).

Finanzes.

Prof. D. Jerome Fisher presented the following treasurer's report:

REPORT OF THE TREASURER COVERING JULY 1, 1959 TO JULY 1, 1960.

Receipts.

Dues for July 1, 1958 - June 30, 1959 *(Note 1).*
Mineralogical Societies of Japan (30) an U. S. S. R. (130) .... 160.—

Dues for July 1, 1959 - June 30, 1960 *(Note 2).*
Mineralogical Societies of Austria (20), Belgium (20), Canada (30), Czechoslovakia (20), Denmark (20), Finland (20), France (70), Germany (50), Great Britain (40), India (20), Italy (40), Japan (30), Netherlands (20), Norway (20), Sweden (40), and the U. S. S. R. (130)................................... 590.—

Dues for July 1, 1960 - June 30, 1961.
Mineralogical Societies of Czechoslovakia (30), Denmark (30), Finland (30), Germany (90), India (30), Italy (60), Norway (30), Spain (30), Switzerland (30), and (the U. S. A. (150) .... 510.—

Total receipts .... 1,260.—

Cash on hand as of July 1, 1959.. 377.35

Grand Total 1,637.35

Disbursements.

President's office *(Note 3).*
Postage 15.98
Printing: Report of Zürich meeting in *Nature*................. 10.38
Printing: Programs for Copenhagen meeting..................... 132.33
Bank Exchange (0.58) and advance from Tresurer (0.73)......... 1.31

                                        Total............... 160.—

Secretary's office.
Postage 66.67
Stationery 8.33
Duplicating.. 12.50
Typist 66.67

                                        Total............... 154.17

Treasurer's office.
Postage 22.38
I. M. A. letterheads (2000)................................... 30.21
Bank charges on draft 1.15

                                        Total............... 53.74

Total disbursements 367.91
Cash od hand as of July 1, 1960........................... 1,269.44

            Grand total (U. S. A. dollars)............... 1,637.35

Respectfully submitted

D. Jerome Fisher
Treasurer

Note 1. Payment of dues by the societies of the other 12 countries represented at Madrid (April 1958) appeared in last year's report.
Note 2. Payment of dues by Spain (20), Switzerland (20), and the U. S. A. (120) appeared in last year's report.
Note 3. Particular attention is called to the fact that the only costs of the Zürich meeting to the Association were printing bills totalling $ 46.29. Outlay on this modest scale was made possible by the hospitality of the town of Zürich, by very generous finalcial aid accorded President Parker by various Swiss firms, and by the voluntary help of numerous people.

OTHER ITEMS.

Auditors.

Adopting the proposal of Prof. Font Altaba, the Delegates appointed Drs. Clausen and Wenk as auditors and scrutineers to the Association for the period of the Second General Business Meeting.

Commissions.

Since several Commissions had meetings later in the day after the Assembly, the President suggested delaying the reports of the Chairmen of the Commissions until the second session of the Business Meeting.

In relation to the question raised in Zürich of merging the Commissions on New Minerals and on Mineral Data, the President informed the Business Meeting that a meeting was held by the Chairmen of both Commissions and that after a fruitful discussion of the different points of view the need of maintaining both Commissions was agreed on. The question of limiting the work of each commission was also decided. Thus the President considered that both Commissions must continue being independent, and this was approved by the Delegates.

Revission of the Constitution.

The following changes in the Constitution were moved and adopted by the delegates:

The last sentence under Article 4 B. The Council, Section *a)* changed to read: Not more than one resident member of any Member Society may be a member of the Council; nor shall any one person hold more than one office.

Article 5. Finances. Delete *consecutive* from the second line of Section *e)*. Add a new Section *f)*. The Member Society shall be re-instated in the membership of the Association and again assume the rights and duties of members after having paid all out-standing dues.

New Commissions.

The President reported on the work of the Committees that studied the desirability of creating new Commissions. The formation of a Commission on the Teaching of Mineralogy (suggested in Zürich) was discussed, and the Delegates agreed that such a Commission should be formed. On the contrary, the President stressed the point that the proposed Commissions on Petrographic Nomenclature and on Meteorites should await the development of the existing commissions in the International Geological Congress, and suggested appointing Liaison Members to both Commissions of the I. G. C., and that they should report in future to the I. M. A.

Prof. Font Altaba suggested the appointment of a Liaison Member to the International Union of Crystallography, and Prof. ORCEL another to the Geochemical Society.

Accordingly, the President was empowered to nominate suitable people for these activities, and the nominations were to be made public for approval at the Assembly in the Second Session of the Business Meeting.

Elections.

The President reminded Delegates of Art. 11 and 12 of the Constitution regarding nominations for elections to the Council.

Publication of Zürich Symposia.

An announcement was made by the President that the papers presented at both Zürich Symposia were already published as an issue of «Estudios Geológicos» in its series «Cursillos y Conferencias» by the Instituto Lucas Mallada Madrid (Spain) and that orders could be placed at the selling price of $ 1.50 (or 90,— Pesetas) to the Secretary.

Next Meeting.

The President called the attention of the Delegates to the possibility of receiving an invitation for the next Meeting of the I. M. A. Prof. Fisher on behalf of the Mineralogical Society of America invited the Association to hold a Meeting in 1962 in Washington, D. C. at a suitable time. After a discussion, the Assembly tendered their hearty thanks to the inviting Society and agreed to hold the meeting at Easter time.

Prof. Guillemin raised the question of the great number of Congresses that are being held, and of the necessity of having longer intervals between Meetings.

The Session was ajourned, to be continued on August 24th. at 9.30 a.m.

SECOND SESSION

The second Session of the Business Meeting of the Delegates was held on August 24th. at 9.30 a.m. at the same place. The President opened the Session by calling the roll of Delegates, after which Business proceeded according to the agenda.

Report by the Auditors.

The Auditors moved the acceptance of the Treasurer's Report as presented. The motion was seconded and accepted unanimously.

The Treasurer explained the financial status of the I. M. A., and suggested that the value of the unit remain at US $ 15.—This was approved.

Reports of the Commissions.

The Chairmen of the four Commissions reported on the work done by their Commissions. All the reports were followed by discussion and accepted. See reports.

Elections.

Having been posted in due time by the Secretary, the following were declared nominated for election as officials of the I. M. A.:

President: D. J. Fisher, M. J. Buerger; 1st. Vice-President: C. E. Tilley; 2nd. Vice-President: D. P. Grigoriev, G. P. Barsanov; Secretary: J. L. Amorós; Treasurer: L. G. Berry; Councillors: P. R. J. Naidu, Th. G. Sahama, H. G. F. Winkler.

Commission on *Abstracts*: Chairman: E. Onorato, M. Fornaseri; Secretary: N. F. M. Henry, R. van Tassel.

Commission on *New Minerals and Mineral Names*: Chairman: M. Fleischer; Secretary: C. Guillemin.

Commission on *Museums*: Chairman: C. Frondel; Secretary: F. Leutwein.

Commission on *Mineral Data:* Chairman: H. Strunz; Secretary: A. Pabst.

Commission on *Teaching:* Chairman: J. Orcel, C. S. Hurlbut; Secretary: H. J. de Wijs.

Chairmen of Liaison Committees: Petrography: C. Burri; Meteorites: D. P. Grigoriev; Geochemistry: W. E. Heinrich; Crystallography: F. Laves.

The election proceeded according to the Bye-Laws. The President explained that the election of those nominees who were uncontested was automatic and required no vote. Prof. Onorato pointed out that he and Prof. Henry were unwilling to serve longer as Chairman and Secretary respectively of the Commission on Abstracts; therefore M. Fornaseri and R. van Tassel were automatically elected as the

officials of this Commission. Votes were cast for the other contested nominations with the following results:

President: D. J. Fisher, 30 votes; M. J. Buerger, 5 votes.
2nd. Vice-President: D. P. Grigoriev, 11 votes; G. P. Barsanov, 21 votes.
Teaching: J. Orcel, 18 votes; C. S. Hurlbut, 15 votes.

Therefore, D. J. Fisher was elected as President, G. P. Barsanov 2nd. Vice-President, and J. Orcel as Chairman of the Commission on Teaching.

After the election the new President took the Chair and after thanking the Delegates and eulogizing the past President declared the meeting was adjourned.

Accordingly, the officials of the the IMA, for 1960-64, are those given below:

OFFICERS.

D. Jerome Fisher, *President.*
  Rosenwald Hall.
  University of Chicago.
  Chicago 37, Illinois.
C. E. Tilley, *First Vice-President.*
  Dept. of Mineralogy and Petrology.
  University, Cambridge, England.
G. P. Barsanov, *Second Vice-President.*
  Mineralogical Museum.
  B. Kalujskaya 16.
  Moscow, U. S. S. R.
José L. Amorós, *Secretary.*
  Museo Nacional de Ciencias Naturales.
  Castellana, 84.
  Madrid, Spain.
L. G. Berry, *Treasurer.*
  Queen's University.
  Kingston, Ont., Canada.

COUNCILORS.

P. R. J. Naidu.
  University of Madras.
  A. C. College Buildings.
  Guindy, Madras 25, India.
Th. G. Sahama.
  Institute of Geology.
  Snellmanink 5.
  Helsinki, Finland.
H. G. F. Winkler.
  Mineralogisches Institut der Universität.
  Deutschhausstr 10.
  Marburg/Lahn, Germany.

Past President.

Robert L. Parker.
  Institute of Technology.
  Sonneggstr. 5.
  Zürich 6, Switzerland.

COMMISSIONS

Abstracts.
  Chairman: M. Fornaseri.
  Secretary: R. Van Tassel.
Mineral Data.
  Chairman: H. Strunz.
  Secretary: G. T. Faust.
Museums.
  Chairman: C. Frondel.
  Secretary: F. Leutwein.

New Minerals and Mineral Names.
  Chairman: M. Fleischer.
  Secretary: C. Guillemin.
Teaching:
  Chairman: J. Orcel.
  Secretary: H. J. deWijs.

COMMITEES

Crystallography.
  Chairman: F. Laves.
Geochemistry.
  Chairman: E. W. Heinrich.

Meteorites.
  Chairman: D. P. Grigoriev.
Petrographic Nomenclature.
  Chairman: C. Burri.

REPRESENTATIVES

Austria: A. Schiener.
Belgium: R. van Tassel.
Bulgaria: I. Kostov.
Canada: L. G. Berry.
Czechoslovakia: J. Sekanina.
Denmark: H. Clausen.
Egypt: E. M. El Shazly.
Finland: T. G. Sahama.
France: C. Guillemin.
Germany: W. von Engelhardt.
Great Britain: C. E. Tilley.

India: K. Rajagopalaswamy.
Italy: M. Fenoglio.
Japan: N. Katayama.
Netherlands: H. J. deWijs.
New Zealand: D. S. Coombs.
Norway: H. Neumann.
Spain: M. Font Altaba.
Sweden: F. E. Wickman.
Switzerland: E. Wenk.
U. S. A.: A. Pabst.
U. S. S. R.: D. P. Grigoriev.

REPORTS OF THE COMMISSIONS

COMMISSION ON ABSTRACTS

Meetings of the Commission.

After a preliminary meeting of five members, plus the General Secretary of the I. M. A. *ex officio,* at Zürich on January 22, 1959, there was a full meeting of the Commission also at Zürich on August 30, 1959. This meeting was attended by delegates from 14 of the 17 member countries of the Commission, along with 10 observers and visitors.

After a full discussion of the problems, the following resolutions were passed unanimously:

(i)   That we should work for the production of Abstracts in our field of science in a single language for western countries.

(ii)   That in principle each country should abstract its own journals and that discussions should be opened with the delegates of the U. S. S. R. to examine the question of an exchange of abstracts.

A Sub-committee was set up to study the details and to establish contact with existing organisations, and it was expected that a report would be ready for the meeting in August, 1960. The members of the Sub-committee are:

Professor Barsanov — U. S. S. R.
Dr. Phemister — Great Britain.
Professor Ernst — Germany.
Professor Winchell — North America.
Professor Wyart — France.

The Chairman and the Secretary of the Commission are members *ex officio,* and Dr. Van Tassel was appointed to the Sub-committee as Vice-secretary.

Meetings of the Sub-committee.

The Sub-committee, with all members present, held a meeting later on August 30, 1959. After discussion of the work to be done, Professor WYART invited the members to meet again in Paris early in the next year.

The second meeting of the Sub-committee was held in Paris on February 6, 1960, the members present being:

Professor Ernst, Professor Wyart, Dr. Hey (replacing Dr. Phemister), Dr. Van Tassel, Dr. Henry, with Dr. Hocart and Dr. Curien as observers from the Société Française de Minéralogie et de Cristallographie. Apologies were received from Professor Barsanov, Professor Winchell and Professor Onorato.

A Draft Plan was worked out for presentation to the Commission.

Chairman's Comments on the Draft Plan.

1.   The Draft Plan presented here is the outcome of several years of meetings, formal and informal, many personal contacts, the exchange of memoranda, and a very large correspondence, all on an international scale. Opinions have been sought from those with most experience in the actual production and editing of abstracts in various fields of science as well as in our own.

2.   There is general agreement that abstracts ought to be international, but, of course, any plan must be organisationally efficient and financially sound. We are handicapped by not having funds of our own with which to launch an international abstracts organisation, but by joining our efforts and our funds it will be possible to make a success of the co-operation that is proposed. It would be easy to raise objections, from one point of view or another, to any plan that could be proposed. But if we are to succeed we must sink our petty differences and we must start working together.

3.   The co-operative idea has the advantage of leaving each country to collect and select its own contribution to abstracts. This new proposal has the additional advantage of leaving the larger countries to manage affairs on a regional basis without interfering with each other but in full co-operation to produce an international publication.

4.   It should be noted that the Sub-committee has found it necessary to depart from the single-language concept accepted in principle at Zürich. This has been done deliberately after full consideration of the technical processes involved. In the opinion of the Sub-committee the advantages of regional editing are so great as to outweigh the disadvantages of tri-lingual publication. It is not too much to expect scientists to be able to read abstracts in their own field in any of the three languages agreed upon, and the difficulty of indexing a trilingual publication is likely to be considerably lessened with the new mechanical methods of indexing that are developing rapidly. The advantages are the reduction of a load of translation and the availability of regional finance and effort towards the production of a publication that would be very costly if all the weight had to fall on the central organisation.

5.   The Sub-committee is well aware of the wisdom of not destroying any well-established organisation in order to set up a new project, however attractive the latter may be on paper in a world that is increasingly conscious of the need for international co-operation. For this reason it has put forward the suggestion that, if the I. M. A. should decide to proceed with this Draft Plan (modified if necessary), then an approach should be made to the Anglo-American organisation with a proposal for joint work over a period of two years without any change of ownership. This would give us the experience of working together without destroying anything, and the Sub-committee firmly believes that this experience would be very successful.

6.   Such a scheme would entail only one major alteration for the Anglo-American Organisation, and that is the change over to photo-reproduction from electrically-typed copy. This procedure has recently been investigated by the Secretary of the Commission, who believes that it offers considerable economies, both in time and in money, for the kind of publication in question.

7.   The Sub-committee stress the need for special funds for the translation of abstracts from the Russian, as this can now only be done on a paid basis. All the work of the Eastern countries is easily available to us, provided that we have the funds for the translation. It is, of course, open to any country of the Eastern group to send their abstracts direct through the I. M. A.

8.   The Sub-committee also proposed a working agreement with the Bulletin Signalétique which could provide a full list of titles which would appear more quickly than would be possible with the fuller abstracts as these would have to be selected and, in the case of

those from the Russian Referativny Zhurnal and from certain other countries, translated also.

9.   Finally the Sub-committee proposed a working agreement between the I. M. A. and the Centre de Documentation in Paris. The Centre is able to supply a photocopy or micro-film of any publication for a small fee, and the I. M. A. organisation could help the Centre to obtain a copy of any paper published in our field of science.

E. ONORATO, Chairman; N. F. M. HENRY, Secretary; R. VAN TASSEL, Vice-Secretary.

COMMISSION ON MINERAL DATA

The Commission on Mineral Data had in Zürich 1959 five working sessions, in Copenhagen 1960 one working session. The meetings were open and guests were welcome; only one or two of the 18 members, or their alternates, of this commission were absent.

Many problems in nomenclature, symbolism and mineral data were discussed; the voting results were in about one third of all items unanimous, also in about one third of the items with one vote against, and in the final third with two votes against. The results were read in the open Business Meeting of IMA in Copenhagen on August 24th 1960 by the chairman and are recomendations of IMA. They are summarized on the Appendix.

The further work of the Mineral Data Commission will be the preparation of an International Mineral Data File, for which the members are invited to submit proposals to the chairman. Further special proposals of the societies should be given by the members of the Mineral Data Commission to the chairman up to June 1st 1961.

G. T. FAUST, Secretary   H. STRUNZ, Chairman

MUSEUMS COMMISSION

The work of the Museum Commission in preparing a World List of Mineral Collections continued during 1959-1960. Representatives of several national societies newly admitted to the IMA were welcomed on the Commission, and were informed as to our activities. The questionnaire approved at the Zurich meeting was printed (through the cooperation of the U. S. National Museum) and copies were made available in bulk to all National committees. The work of compiling the separate National lists of collections has been

completed or is nearing completion in a number of countries, but much work still remains to be done. The size of the task is illustrated by the fact thet the U. S. national committee alone has already obtained data on about 600 collections. Possibly several years will be required before the whole project can be completed.

At the Copenhagen meeting discussion will be made of specific problems encountered during the compilation of the data, with particular regard to coverage and completeness of response. Specific plans also will be discussed for beginning the second main project of the Commission, that of preparing a finding-list of type specimens.

F. LEUTWEIN, Secretary   C. FRONDEL, Chairman

COMMISSION ON NEW MINERALS AND MINERAL NAMES

The Commission has suffered a great loss in the death of Prof. Ciro Andreatta, representing Italy.

The Commission has been active by correspondence. The following topics are on the agenda for the Copenhagen meeting (name of person preparing a report in parentheses):

1.   Statement of purposes of Commision (Fleischer, U. S. A.).
2.   Preparation of definitions of mineral, mineral species, varieties, mineral groups (D. P. Grigoriev, U. S. S. R.).
3.   Statement of what should be required in the description of a new mineral (F. Fermingeat, France).
4.   Unification and rationalization of mineralogical nomenclature (M. H. Hey, Great Britain).
5.   Possibility of review, before publication, of suggested new mineral Names (W. P. DE ROEVER, Netherlands).
6.   Reviews of published new names. Possibility of publication of lists of approved and disapproved names (C. Guillemin, France).

The Commission is also organizing a discussion of the nomenclature of feldspars in conjunction with the I. M. A. Symposium, and will participate in the discussion of Clay Mineral Nomenclature sponsored by the British Clay Minerals Group. A meeting with Prof. Strunz, to correlate the work of the Commisions on Mineralogical Data and New Minerals will be held in Zürich early in August.

MICHAEL FLEISCHER, Chairman.

APPENDIX

RECOMMENDATIONS OF THE COMMISSION ON MINERAL DATA

1)   METRIC DATA *(from lattice and morphology)*

cell dimensions: a_o, b_o, c_o (in metric $\text{Å} = kX : 1,002$; «Internationale Tabellen zur Kristallstrukturbestimmung 1936» give kX!);

axial ratios, from cell dimensions: $a_o : b_o : c_o$

axial ratios, from morphological measurements: $a : b : c$ (since 150 years!);

interaxial angles: α, β, γ.

orientation: Triclinic, reduced cell (shortest three translations) with $c < a < b$, with α and β obtuse (γ cannot be chosen obtuse or acute at will; its character follows from the proceeding conditions);

Monoclinic, shortest two translations in plane (010), with $c < a$; β obtuse (stumpf).

Orthorhombic, axes along symmetry directions, with $c < a < b$;

Tetragonal, smallest cell;

Hexagonal-P, smallest hexagonal cell;

Hexagonal-R, smallest hexagonal cell with extra nodes at $\dfrac{121}{333}$ and $\dfrac{212}{333}$;

Cubic, no recommendations necessary.

X-ray reflections:	hkl;
crystal face indices:	(hkl), hexagonal: (hkil);
crystal form indices:	}hkl{;
crystal zone indices:	[uvw];
crystal zone form indices:	⟨uvw⟩ (in carets)
combination of forms (Tracht):	}hkl{ · h'k'l' · h"k"l" ....;
habit (Habitus):	dominant forms; isometric (equant) (1), tabular, acicular, ...;
microscopic morphology and electronmicroscopic morphology	are to be encouraged
interplanar (lattice) spacings.	d-values; d_{hkl}, from X-ray powder patterns, indexed whenever possible, with intensities 0-10 (est. or calibr.), «est.» means estimated visually, «calibr.» means compared with calibrated scale.

2) SYMMETRY DATA *(from lattice and morphology).*

The 7 symmetry systems:

I.	Triclinic.	(Triklin).
II.	Monoclinic.	(Monoklin).
III.	Orthorhombic.	(Rhombisch).
IV.	Tetragonal.	(Tetragonal).
V.	Hexagonal-Rhombohedral.	(Hexagonal-Rhomboedrisch).
VI.	Hexagonal.	(Hexagonal).
VII.	Cubic.	(Kubisch).

The 32 symmetry classes:

I.	1)	Triclinic-pedial.	(Triklin-pedial).
	2)	" -pinacoidal.	(" -pinakoidal).
II.	3)	Monoclinic-sphenoidal.	(Monoklin-sphenoidisch).
	4)	" -domatic.	(" -domatisch).
	5)	" -prismatic.	(" -prismatisch).
III.	6)	Rhombic-disphenoidal.	(Rhombisch-disphenoidisch).
	7)	" -pyramidal.	(" -pyramidal).
	8)	" -dipyramidal.	(" -dipyramidal).
IV.	9)	Tetragonal-pyramidal.	(Tetragonal-pyramidal).
	10)	" -disphenoidal.	(" -disphenoidisch).
	11)	" -dipyramidal.	(" -dipyramidal).
	12)	" -trapezohedral.	(" -trapezoedrisch).
	13)	Ditetragonal-pyramidal.	(Ditetragonal-pyramidal).
	14)	Tetragonal-scalenohedral.	(Tetragonal-skalenoedrisch).
	15)	Ditetragonal-dipyramidal.	(Ditetragonal-dipyramidal).
V.	16)	Trigonal-pyramidal.	(Trigonal-pyramidal).
	17)	" -rhombohedral.	(" -rhomboedrisch).
	17)	" -trapezohedral.	(" -trapezoedrisch).
	19)	Ditrigonal-pyramidal.	(Ditrigonal-pyramidal).
	20)	" -scalenohedral.	(" -skalenoedrisch).
VI.	21)	Hexagonal-pyramidal.	(Hexagonal-pyramidal).
	22)	Trigonal-dipyramidal.	(Trigonal-dipyramidal).
	23)	Hexagonal-dipyramidal.	(Hexagonal-dipyramidal).
	24)	" -trapezohedral.	(" -trapezoedrisch).
	25)	Dihexagonal-pyramidal.	(Dihexagonal-pyramidal).
	26)	Ditrigonal-dipyramidal.	(Ditrigonal-dipyramidal).
	27)	Dihexagonal-dipyramidal.	(Dihexagonal-dipyramidal).

(1) «isometric» is more international!

VII. 28) Tetartohedral.   (Tetartoedrisch).
      29) Diploidal.   (Disdodekaedrisch).
      30) Gyrohedral.   (Gyroedrisch).
      31) Hextetrahedral.   (Hex'tetraedrisch).
      32) Hexoctahedral.   (Hex'oktaedrisch).

The 230 symmetry groups (space groups):

space group symbols, f.e.

$$D_{2h}^{16} - Pnma \qquad D_{2h}^{16} - Pmcn$$

$$D_{2h}^{16} - Pnam \qquad D_{2h}^{16} - Pmnb$$

$$D_{2h}^{16} - Pbnm$$

$$D_{2h}^{16} - Pcmn,$$ (100) glide plane with
                                glide components $c_o/2$
                         (010) mirror plane
                         (001) glide plane with
                                glide components $a_o/2 + b_o/2$

(SCHOENFLIES-symbol D_{2h}^{16} is not to be modified, MAUGUIN-symbol is to be modified from X-ray extinctions; metric orientation has priority!).

Threefold and sixfold inversion axes in stereographic projections (fig. 1);

The symmetry center in stereographic projections (fig. 2);

In «Internationale Tabellen zur Kristallstrukturbestimmung» (1936) and «International Tables for X-ray Crystallography» (1952) the meaning of the old morphological symbol unfortunately was changed; as it has now two meanings, it should be dropped; IMA gives the proposals fig. 1 and 2 to the IUC.
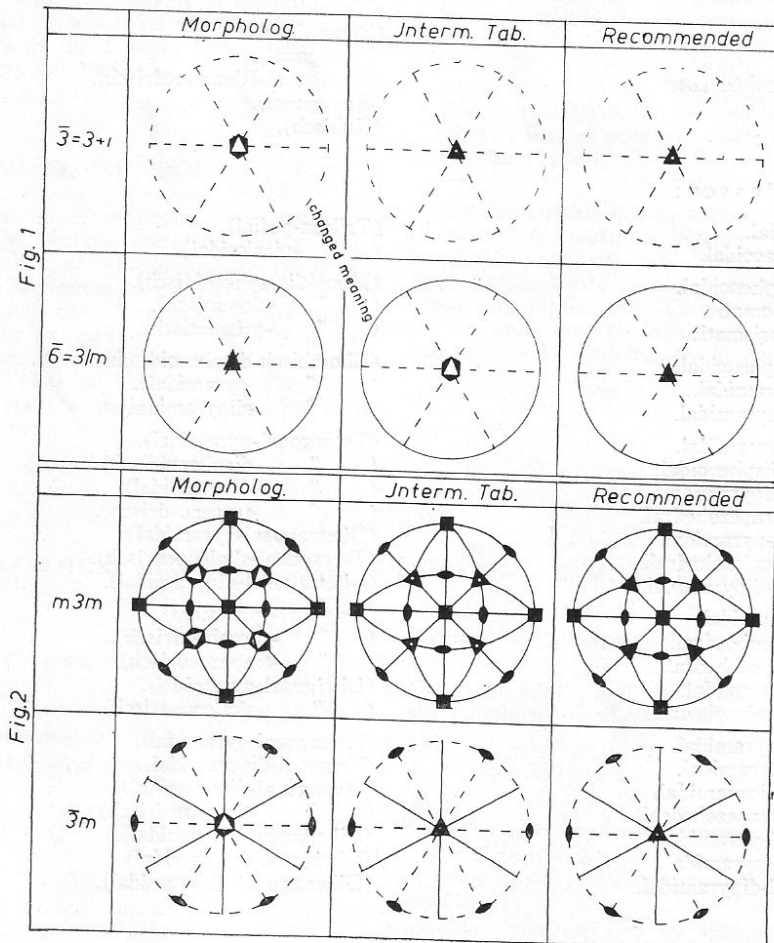
3) PHYSICAL DATA

cleavage:

hardness: H
density (corrected for temperatur): $D = g/cm^3$ (D_x, calculated from X-ray data)
specific gravity: G
color: ....,......
luster: ....,......
streak: ....,......
infra-red data: ....,......
ultra-violet data: ....,......
fluorescence: ....,......

4) OPTICAL DATA

	refractive indices	axes of Fresnell ellipsoid
cubic	n	$V \; (V = \dfrac{1}{n})$;
uniaxial	ε, ω;	$E, O \; (E = \dfrac{1}{\varepsilon}, \; O = \dfrac{1}{\omega})$;
biaxial	α, β, γ;	$X, Y, Z \; (X = \dfrac{1}{\alpha}, \; Y = \dfrac{1}{\beta}, \; Z = \dfrac{1}{\gamma})$;

birefringence (max): $\varepsilon - \omega$; $\gamma - \alpha$;
optical angle: $2V \; (+)$, $2V \; (-)$; $(2V_\gamma, 2V_a)$;
extinction angle: $Z \wedge c \; (Z : c)$.

Opaque minerals

Polishing:
Reflectivity: R_m (medium), R_r (red), R_{or} (orange), R_v (yellow), R_{bl} (blue), R_{viol} (violet);
Reflexion color: ....
Reflexion pleochroism: ....,........
Etching behaviour: ....
Microchemical reactions and staining: ....
Texture, intergrow hs: ....

5) CHEMICAL DATA

Formulae (as simple as possible, for special purposes brackets and coordination numbers may be used):
Proposals 5-b, -c, -d, -e, -f open for further discussion.

a) **with noncomplex anions**: no recommendation necessary.

b) **with komplex anions**:

calcite $\qquad$ $CaCO_3$ or $Ca[CO_3]$
dolomite $\qquad$ $CaMg[CO_3]_2$
olivine $\qquad$ $(Mg,Fe)_2SiO_4$ or $(Mg,Fe)_2[SiO_4]$
garnet $\qquad$ $Ca_3Al_2[SiO_4]_3$.

c) **with mixed anions**:

malachite $\qquad$ $Cu_2[(OH)_2|CO_3]$
chlor-apatite $\qquad$ $Ca_5[Cl|(PO_4)_3]$
kyanite $\qquad$ $Al_2[O|SiO_4]$
muscovite $\qquad$ $KAl_2[(OH)_2|AlSi_3O_{10}]$
(OH, Cl, O etc. are linked only to the cations, they are to be written b e f o r e the complex ions).

d) **structural formulae with coordination numbers**:

calcite $\qquad$ $Ca^{[6]}[CO_3]$ $\qquad$ aragonite $Ca^{[9]}[CO_3]$

malachite $\qquad$ $Cu^{[2+4]}Cu^{[4+2]}[(OH)_2|CO_3]$

fluor-apatite $\qquad$ $Ca_2^{[o+6]}Ca_3^{[1+5]}[F|(PO_4)_3]$

garnet $\qquad$ $Ca_3^{[8]}Al_2^{[6]}[SiO_4]_3$

topaz $Al_2{}^{[2+4]}[F_2|SiO_4]$

muscovite $K^{[0+12]}Al_2{}^{[2+4]}[(OH)_2|AlSi_3O_{10}$

e) the water in mineral formulae:

hydrogen ions, H^+:   nahcolite $Na[CO_2OH]$ or $NaH[CO_3]$

                                 mercallite $K[SO_3OH]$ or $KH[SO_4]$.

hydroxyl ions, $(OH)^-$:   malachite $Cu^{[2+4]}Cu^{[4+2]}[(OH)_2|CO_3]$

                                 alunite $K^{[6+6]}Al_3{}^{[4+2]}[(OH)_2|(SO_4)_2$.

coordination water, H_2O: thermonadrite $Na^{[5+1]}Na^{[4+2]}[CO_3]\cdot H_2O$

                                 chalcanthite $Cu^{[2+4]}[SO_4]\cdot 5H_2O$

                                 blödite $Na_2{}^{[4+2]}Mg^{[3+3]}[SO_4]_2\cdot 4H_2O$

hydroxyl ions *and* coordination water:

                                 callaghanite $Cu_2{}^{[401]}Mg_2{}^{[411]}[(OH)_6|CO3]\cdot 2H_3O$.

interlayer water $\left.\begin{array}{c}\overline{}\\ H_2O \end{array}\right\}$:   montmorillonite $\left\{ \begin{array}{c} (Al,Mg)_2{}^{[2+4]}[(OH)_2|Si_4O_{10}]^{0,33-} \\ Na^+_{0\cdot33}\;(H_2O)_4 \end{array} \right\}$

zeolitic water, $+ H_2O$:   natrolite $Na_2[Al_2Si_3O_{10}]+2H_2O$.

hydroxyl ions *and* zeolitic water: pharmacosiderite $K^{[?]}Fe_4{}^{[330]}[(OH)_4|(AsO_4)_3]+6H_2O$.

hydroxyl ions, coordination water *and* zeolitic water: palygorskite

$$Mg_3{}^{[2400]}Mg_2{}^{[0420]}[(OH)_2|Si_4O_{10}]_2\cdot 4H_2O+4H_2O$$

sepiolite, gunnbjarnite

$$(Mg,Fe)_6{}^{[2400]}Mg_2{}^{[0240]}[(O,OH)_2|Si_6O_{15}]_2\cdot 4H_2O+8H_2O$$
$$800^0C450^0250^0$$

absorption water, $+$ aqu.: opal SiO_2+n aqu.

---

f) $(OH)_4$ for SiO_4 (etc.):

symbol of vacant sites $|\square|$: hydroxylgarnet $Ca_3Al_2[(SiO_4)_{1-x},(|\square|(OH)_4\overline{x}]_3$

                coffinite $U[(SiO_4)_{1-x},(|\square|(OH)_4)_x]$

Sequence of cations according to ionic radii decrease; in diadochic substitution according to abundance.
Formulae units in unit cell: Z.

g) Chemical Analysis etc.

Thermal Analysis: ....

Differential Thermal Analysis: ....

Solubility in water: ....

Solubility or decomposition in water in acids or alcalies: ....

Etching behaviour: ....

Blowpipe behaviour: ....

Microchemical reactions and staining: ....

Ion exchange power: ....

Fusibility: ....

Melting constants: ....

Modifications: ....

6) ATOMIC STRUCTURE OF MINERALS

Crystal structure and crystal chemistry: ....

Crystal structure and morphology: ....

Crystal structure and physical properties: ....

Crystal structure and chemical behaviour: ....

7) Occurrences and Alterations in Nature

Geochemical sequence: ....
Paragenesis: ....
Alterations: ....
Occurrences, deposits: ....
Deposits of economic value: ....
Mining: ....
Topographic mineralogy: ....

8) Mineral Classification

Alphabetical arrangement: yes; for and index decimal-cla sification, arranged chemically; yes, for a special use classification on crystal chemistry: yes (Mineralogische Tabellen, in addition: solenosilicates).

9) International Mineral Data File.
(Proposal, open for further disccusion.)

Content:
Size of form sheets:
Organization:
References:
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DANA, The System of Mineralogy (Silica Volume in press, Nesosilicates Volume almost ready, FRONDEL).
STRUNZ, Mineralogische Tabellen (a Russian Edition in press, an English Edition in preparation).
HEY, Chemical Index of Minerals (2nd Edition).
CHUKHROV (& ALIES), Minerals (in Russian, Volume I, Elements and Sulfides, just came out).
FLEISCHER, New Minerals (American Mineralogist).
GUILLEMIN, and PERMINGEAT, Revue des espèces minerales nouvelles (Bull. soc. franc. crist. min.).
BOHNSTEDT-KUPLETSKAYA, Neue Mineralien (Zapiski Vses Mineralog. Obshch.).

PRELIMINARY ANNOUNCEMENT 1962 MEETING WASHINGTON, D. C.

SCHEDULE

Northern Field Trip (New York-Washington) ... ... April 14-16, 1962
Washington Meeting ... ... April 17-20, 1962

Commission meetings	April 17	
Scientific sessions	April 18-20	at U. S. National Museum
Reception welcome	April 17	at Marriot Motor Hotel, 5 P. M.
Dinner	April 19	at Marriott Motor Hotel, 7 P. M.

Southern Field Trip (Washington-Virginia-Washington)
April 20-22, 1962

Preliminary plans (as of April 1961) for the 1962 meeting of the International Mineralogical Association in Washington, D. C. have been formulated as outlined in the schedule above. April is one of the busiest months of the year in Washington as far as visitors are concerned and we have been fortunate in being able to reserve accomodations and other facilities at the Marriott Motor Hotel, on the Potomac River in Virginia. The Local Committee (Alvin Van Valkenburg, Chairman. National Bureau of Standards, Washington 25, D. C.) is planning to provide accomodations for the majority of visitors from outside the country through the hospitality of scientists residing in the Washington area. Various activities for accompanying family members are being planned under the direction of Kathleen Roedder. The Mineralogical Society of America has applied for financial assistance toward travel for participants, field trips, and publication expenses for the meeting, and as soon as it is known to what extent these funds may be available, a more definite notice will be distributed with information on the costand other details.

The scientific sessions will include at least two symposia: *A.* Sulfides (Chairman: Professor A. J. Frueh, Jr. of McGill University) and *B.* Layered Intrusions (Chairman: Professor C. E. Tilley of Cambridge University).

INTERNATIONAL MINERALOGICAL ASSOCIATION

FIELD TRIPS

Northern Field Trip   Leader: Paul F. Kerr   April 14-16, 1962

April 14: New York City. Visits to the American Museum of Natural History, Columbia University Department of Geology, and Lamont Geological Observatory.

April 15: Paterson, New Jersey (zeolites) and Franklin Furnace, New Yersey (zinc).

April 16: Cornwall, Pennsylvania (sphalerite, magnetite, etc.).

Total cost will not exceed $50.00 including transportation, lodging, and food.

Southern Field Trip   Leader: Richard V. Dietrich   April 20-22, 1962

Leave Washington early evening of April 20 for Amelia Court House, Virginia, arriving later in the evening.

April 21: Amelia Court House (pegmatite), Willis Mountain (kyanite), and Roseland (rutile).

April 22: Miscellaneous Virginia localities (unakite, clay, bauxite, manganese) Luray Caverns.

Total cost will not exceed $50.00 including transportation, lodging, and food.

Museum Trip.

April 21-24: Visit to museums in Washington Philadelphia, New York, New Haven, and Cambridge; details will be supplied later.

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Los trabajos entregados para su publicación serán revisados por la Comisión de Redacción del Instituto «Lucas Mallada», la cual decidirá sobre su publicación. Los autores procurarán atenerse a las siguientes normas:

TEXTO.—El texto se entregará redactado en forma definitiva, en hojas mecanografiadas a doble espacio, por un solo lado y con márgenes amplios.

Si en el trabajo existieran figuras o cuadros es conveniente dejar un pequeño espacio en blanco con la indicación del número de la figura o del cuadro en la zona aproximada donde sea más conveniente intercalar la figura o cuadro. También puede indicarse esta posición en los márgenes del texto.

Todos los trabajos estarán acompañados de un resumen cuya extensión no podrá superar al 15 por 100 de la del texto. En los trabajos escritos en español este resumen se traducirá al inglés; en los escritos en idioma extranjero (con preferencia inglés o francés), el resumen será traducido al español. La traducción será realizada por la Redacción en caso de que el autor no la efectúe.

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En las referencias bibliográficas dentro del texto se indicará el autor y año de publicación, y si es necesario la página del trabajo a que se hace referencia.

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ó 170 mm. (ancho de columna y de doble columna, respectivamente). Sólo en casos especiales (mapas, p. e.) se sobrepasará esta última dimensión. En las ilustraciones a escala, ésta se expresará solamente en forma gráfica, con objeto de evitar errores en caso de que el dibujo original sea reducido.

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La explicación de las figuras se entregará en hoja u hojas incluídas al final del texto.

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Las pruebas serán devueltas en el plazo máximo de quince días. Transcurrido este plazo la Redacción decidirá entre retrasar el trabajo para un número siguiente o realizar ella misma la corrección, declinando la responsabilidad por los errores que pudieran persistir.

La Redacción efectuará una nueva corrección de 2.as pruebas para cerciorarse de que han sido cumplidas las correcciones del autor.

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