PROCESSES LEADING
TO EQUILIBRIUM
IN FELSPAR SYSTEMS

by

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Summary

Barth (1956) proposed that the partitioning of Na and Heier (1960) that the partitioning of Sr, between coexisting felspars, could be used for geothermometry. The present thesis examines not only the partitioning of these elements between felspars from granites but also between synthetic felspars formed in closed hydrothermal systems. Although equilibrium partitioning in the synthetic systems could not be proven the experimental results are consistent both with data on natural metamorphic felspars and with Barth's predictions. The results are interpreted on the basis of published crystal structures.

For the granites the partition ratios have been compared with temperature data deduced from either muscovite-paragonite relationships:- for those granites which contained a white mica, or from sphalerite-pyrrhotite relations:- in the case of a sample taken from adjacent to the lode at Broken Hill, N.S.W.. The distribution modes for sodium, in the case of the mica containing granites, do not enable temperatures which correlate with those from the micas, to be deduced from the Barth geothermometer. In addition a sequence of the sodium partition ratios can not be correlated with a sequence

of the strontium ratios. These negative results are believed to be explicable in terms of i) crystallographic data, published since Eugster's (1955) data, on muscovite-paragonite solid solutions,

ii) lack of equilibrium in granite systems,
iii) effects of bulk composition.

Barth's hypothesis that the partitioning of strontium between coexisting felspars should be temperature sensitive was supported by very little evidence until work in this department by Virgo (1966), on a series of felspars from rocks of increasing metamorphic grade, showed a correlation between grade and the partitioning ratio for strontium (calculated as

$$\frac{\text{mol\% strontium felspar in alkali felspar}}{\text{mol\% strontium felspar in plagioclase}}).$$

This correlation suggested that experiments to further test the hypothesis that, with increasing temperature the potassium felspar lattice takes in higher concentrations of strontium than the coexisting plagioclase lattice, would be useful to substantiate an observation with interesting crystal chemical implications.

Investigation~~s~~ of the above hypothesis involved building hydrothermal apparatus in which the partitioning of strontium and the alkali metals between coexisting felspar phases could be achieved at a series of temperatures.

The temperatures were in the range 500°-880°C. Although equilibrium has not been proven the results confirm that the distribution ratios for strontium increase with temperature up to about 700°C, but above this value the ratios fall with increasing temperature.

These observations are explained in terms of a model which takes into account the change with temperature, of the ~~elliptical~~ ellipsoidal free space about the large cations in plagioclases and alkali felspars. The choice of this model is further confirmed by the way in which it explains published data on volume and linear expansion of felspars.

Incidental to the partition studies, the experimental results for the An-Or-Ab-H_2O-$SrCl_2$ system, investigated, have shown i) that three and perhaps four subsolvus felspars can coexist under subsolvus conditions, and ii) that the potassium content of plagioclases is sensitive to temperature of formation.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University; nor, to the best of my belief, does the thesis contain any material previously published or written by another person, except where appropriate reference is made in the text.

P.G. Slade,

Signed:

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CHAPTER I

PREVIOUS WORK

Introduction

The theoretical variation of distribution coefficients (K_T) of a solute between two solvents, with the temperature (T), in degrees absolute, is given by the Nernst equation:-

$$(1) \qquad K_T = K_o e^{-\frac{E}{RT}}$$

$$\text{or} \quad \ln K_T = -\frac{1}{T}\frac{E}{R} + \ln K_o$$

where E is the difference in energy, at temperature T, between one mol of the solute dissolved in solvent 1 and one mol of that solute dissolved in solvent 2, R is the gas constant, and K_o is the coefficient in the notational standard state. Barth (1956) showed that if alkali felspar and plagioclase are regarded as solid solvents for albite, the composition of the felspars affects the energy E and thus changes the coefficient of distribution of albite. He suggested that the following relationship could be applied, if adjusted for different compositions of the felspar phases:-

$$\frac{\text{mol fraction of albite in alkali felspar}}{\text{mol fraction of albite in plagioclase}} = \text{A constant } (Kd_{Ab}) \text{ at a given temperature.}$$

Barth correlated Kd_{Ab} with an empirically determined temperature scale over the range 350°-1000°C. This geothermometer has been criticized by a number of authors (Dietrich, 1961, presents the major criticisms).

Barth (1961) stressed the idea that trace elements would be likely to partition between coexisting felspars according to equation (1). Work by Heier (1960) was used by Barth to illustrate the importance of the partitioning of Sr. It is one of the aims of this thesis to examine more closely the partitioning behaviour not only of Sr but also of Na.

The rest of the present chapter will be concerned with a brief resumé of published experimental work relating to the Barth geothermometer, as well as presenting in more detail some unpublished results, obtained by D. Virgo, of the Geology Department in the University of Adelaide, on coexisting felspars from middle amphibolite and granulite facies rocks.

I <u>Earlier Experimental Work</u>

a) Winkler (1961), using starting materials prepared from illite-containing clays, determined the compositions and Kd_{Ab} values for felspars formed in the temperature range 620°-720°C and at a pressure of 2000 bars. The only significant composition differences in the starting materials were with respect to the Na_2O content. Table 1 gives the results of Winkler's experiments. From these results he arrived at the following conclusions.

1) For starting material of a given composition the Kd_{Ab} values did not show any variation, with the temperature range investigated.

2) The Kd_{Ab} values were considerably influenced by different soda contents in the starting materials. Winkler (1961) further showed that other major constituents of a rock influence the felspar compositions.

b) Orville (1962) reported results of exchange reactions between a potassium felspar phase and alkali chloride solutions. He concluded that only in the potassium felspar composition-range Or_{95}-Or_{85} are the tie lines independent of composition in the alkali chloride-potassium felspar system. For a series of experiments, at temperatures of 500°, 600° and 700°C and different bulk compositions, Orville deduced that Kd_{Ab} values change with temperature but the Kd_{Ab} values overlap at different temperatures.

c) Yoder, Stewart and Smith (1957) determined the compositions of coexisting K-felspar and plagioclase in equilibrium, at P_{H_2O} of 5000 bars at 720°,

Table 1. Albite component in coexisting felspars of high grade metamorphites, derived from illitic clays, with deduced distribution coefficients and corresponding temperature ranges. (Winkler, 1961).

Ab-component (mol%)		Kd_{Ab}	Temperature °C	Bulk Na_2O (wt%)
K-felspar	Plagioclase			
2.5	42	.06 ± .02	670, 675, 700	.43
8.5	68	.13 ± .02	650, 670, 700, 710, 720	1.36
19.0	75	.25 ± .02	620, 630, 650, 670	2.11

and 770°C, with a liquid and a gas phase. These compositions are given in Table 2, along with the Kd_{Ab} values deduced from them. As can be seen Kd_{Ab} values decrease with increasing temperature. Although this is opposite to Barth's prediction, the explanation can be seen from Yoder et al. (op. cit.) figures 36 and 37. Temperatures and pressures in Yoder's experiments were such that felspar compositions on the solidus surface were in equilibrium with liquid compositions on the liquidus surface. Under these circumstances a decrease in temperature will result in an increase of the albite content of both K-felspar and plagioclase. At subsolidus temperatures however, and at the same P_{H_2O}, the albite contents will fall with decreasing temperature and the trends which Barth predicted will be followed. Most regional metamorphism is thought to involve recrystallization of felspars under subsolidus conditions.

d) Steuhl (1960) determined the composition of coexisting felspars in a paragneiss at P_{H_2O} of 2000 bars and in a temperature range 550°-700°C. He found the variation of the albite distribution coefficient with temperature was more complex than any variation predicted by the Nernst distribution law.

e) Eugster (1955) determined the partitioning ratio of cesium and potassium between H_2O vapour and potassium

Temperature	Felspar Component	K-felspar	Plagioclase	Kd_{Ab}
770°	Or	92.50	3.75	
	An	1.87	56.25	.138
	Ab	5.63	40.00	
720°	Or	78.75	3.75	
	An	1.25	22.50	.264
	Ab	20.00	73.75	

Table 2.

Coexisting felspar compositions, determined experimentally by Yoder, Stewart and Smith (1957), and Kd_{Ab} values calculated from them.

felspar crystals for very low concentrations of cesium relative to potassium at 1,000 and 2,000 bars pressure and at temperatures from 500°C-800°C. The experimental data of Eugster can be plotted on a diagram with ln K_T and $\frac{1}{T}$ as coordinates;

$$K_T = \frac{Cs_{(s)} \cdot K_{(g)}}{K_{(s)} \cdot Cs_{(g)}}$$, where the subscripts (g) and (s) refer to gas and sanidine phases respectively, and T is the absolute temperature. This diagram is linear over a considerable temperature range, indicating that for dilute solutions equation (1) is obeyed.

II The Work of D. Virgo

The work of Virgo (1966) is given here in some detail since not only is it at present unpublished but also because it produced encouraging results relating to the Sr-felspar geothermometer, as well as suggesting that Na distribution is an unreliable indicator of metamorphic grade. The work is considered according to rock types investigated.

a) Almandine-amphibolite and granulite facies rocks from Ceylon, Broken Hill (New South Wales) and the Musgrave Ranges (South Australia). Also discussed are data for rocks of this grade from the Adirondack Lowlands, Engel and Engel (1960) and from Langöy, Heier (1960).

b) Rocks of the sillimanite-muscovite and sillimanite-orthoclase subfacies of the almandine amphibolite facies regions near Adelaide, South Australia.

In all areas, with the exception of the Musgrave Range area, mapping had been carried out in sufficient detail to delineate an isograd between two facies. In the Musgrave Range area, although their extent in area was not known, mineralogical differences enabled specimens representative of the two facies present, to be obtained. The materials selected by Virgo were in all cases 4-5 cms in diameter:- to ensure local equilibrium prevailed throughout, Kretz (1961), and obvious polymetamorphic effects were avoided. After careful purification of the coexisting felspars the elements Na, K, Ca, Ba, Sr and Rb were determined by methods similar to those discussed in chapter 2.

The distribution modes for Na and Sr were graphically expressed in terms of distribution or Roozeboom diagrams, Kretz (1959) p 379. The mol percent albite in the plagioclase was plotted against mol percent albite in the alkali-felspar, similarly for the strontium felspar component. For an equilibrium partitioning of a component between the coexisting phases points in these plots define a straight line when:-

i) the partitioning component forms a dilute solid solution in both phases,

and ii) both phases are ideal for the partitioning element.

Slopes of the lines, defined by the point-plots vary with changes in the physical conditions under which partitioning took place. With this background the relationships which Virgo found between the distribution coefficients for sodium felspar and strontium felspar with metamorphic grade can now be examined.

a) Sodium felspar distribution coefficients:

Fig. 1(a), (b), (c), (d) and Fig. 2(a) are taken from Virgo (1966) and present his data for the granulite-amphibolite facies areas. From these plots it can be seen that there exists a considerable scatter of distribution coefficients even for isofacial rocks. It can also be seen that different Kd_{Ab} values exist for the metamorphic zones represented. Fig. 2(b), (c) and (d) give the data for the almandine-amphibolite facies felspars and show how the sodium distribution coefficients scatter considerably while not clearly reflecting metamorphic

Fig. 1 from Virgo (1966).

(a) refers to the Broken Hill area.

(b) refers to the Musgrave Range area.

(c) refers to the Ceylon area.

(d) refers to the Adirondack Lowlands area.

● refers to Granulite Facies.

○ refers to Almandine Aphibolite Facies.

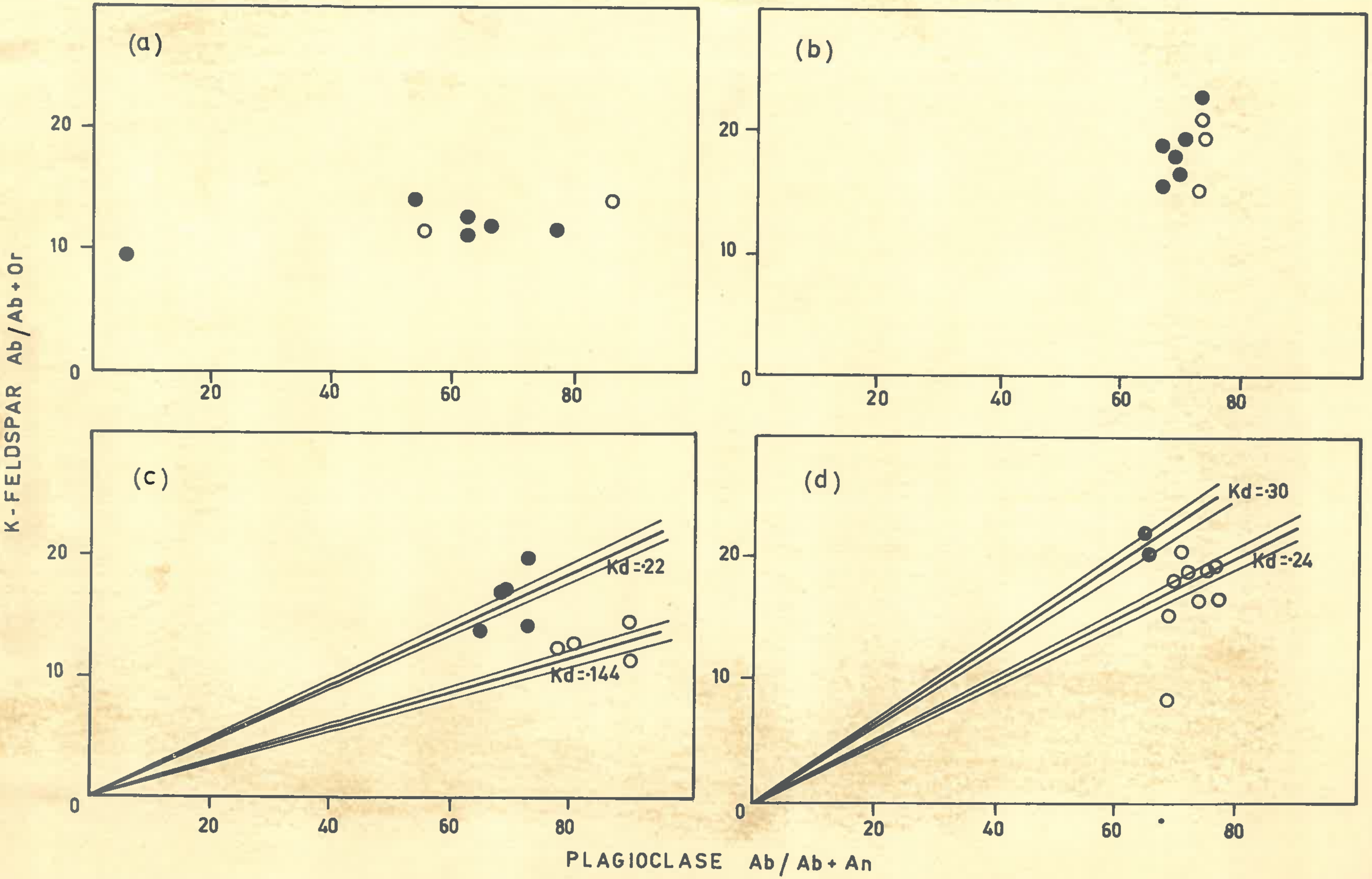


FIG. 1. DISTRIBUTION OF ALBITE BETWEEN K-FELDSPAR AND PLAGIOCLASE

Fig. 2 from Virgo (1966).

(a) refers to the Langöy area.

(b) refers to the Pewsey Vale area.

(c) refers to the Springton area.

(d) refers to the Palmer (P) and Reedy
Creek (R.C.) area.

(These last three areas are near Adelaide, South Australia).

In 2(a) △ refers to Granulite Facies.
● refers to Granulite Facies.
+ refers to Retrograde samples.
× refers to Transitional rocks.
○ refers to Upper Almandine Aphibolite.
Q refers to Lower Almandine Aphibolite.

In 2(b) ● refers to Sillimanite almandine
K-felspar subfacies.
+ refers to Sillimanite almandine
muscovite subfacies.

In 2(c) and 2(d)
● Upper sillimanite-almandine muscovite
subfacies.
+ Lower sillimanite-almandine muscovite
subfacies.

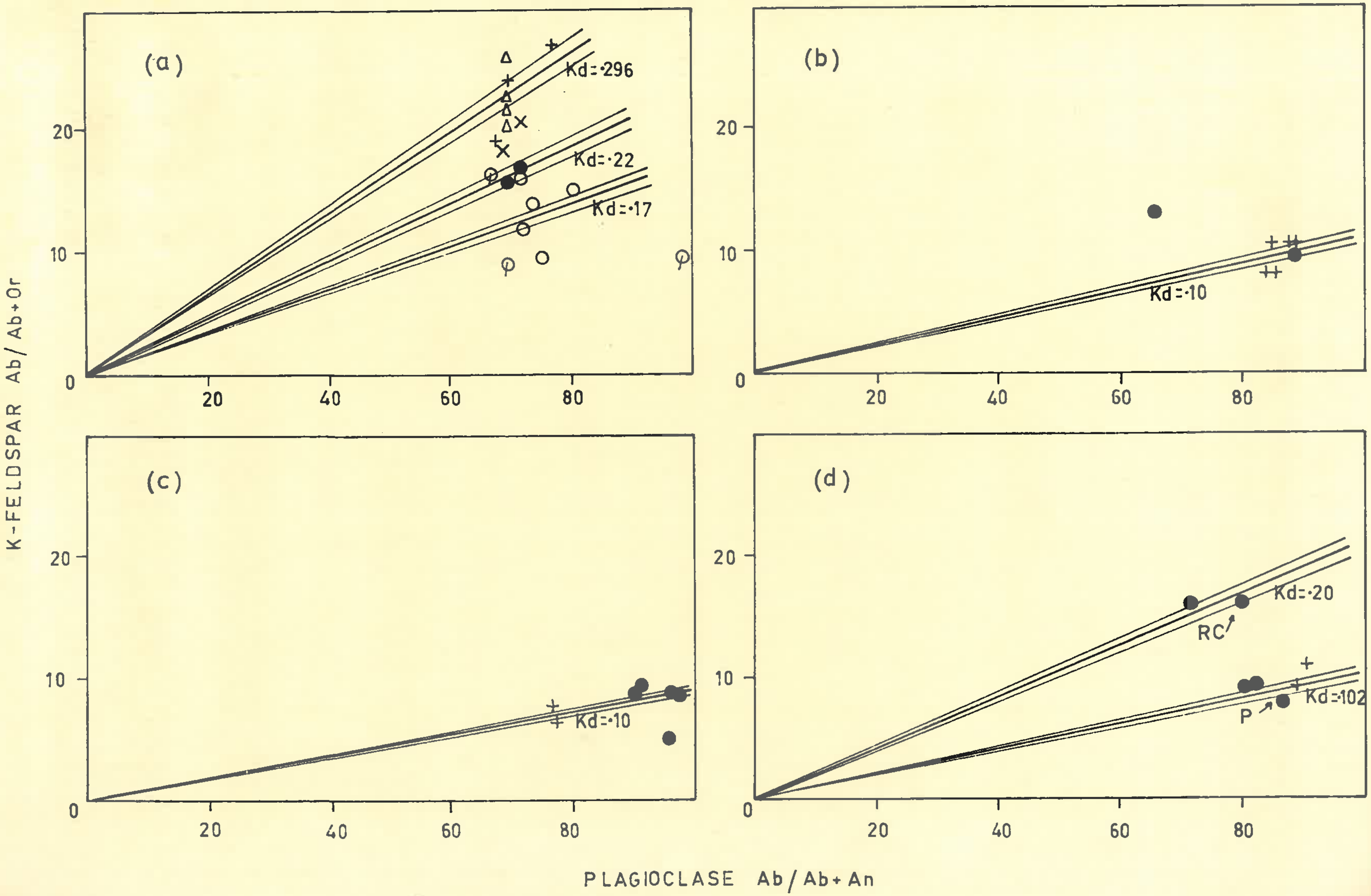


FIG. 2. DISTRIBUTION OF ALBITE BETWEEN K-FELDSPAR AND PLAGIOCLASE

grade. The data presented in Figs 1 and 2 led Virgo to the conclusion that sodium distribution was an unreliable indicator of metamorphic grade and that bulk composition of the crystallizing rocks was critically important.

b) Strontium felspar distribution coefficients: Figs 3,4,5, and 6 present Virgo's data on strontium partitioning in felspars from the Musgrave Range, Broken Hill, Ceylon and Langöy area metamorphics. On each diagram an average distribution coefficient, as well as a ±5% percent range in the distribution coefficient (Kd_{SrF}) is shown for isofacial rocks. (±5% represents the estimated total error). From Figs 3 to 6 the following significant features are recognisable.

1) Points fall close to a straight line passing through the origin (departures from the ±5% range have features discussed below).

2) The regularity of partitioning is taken as an indication that chemical equilibrium was realized during metamorphism.

3) There seems to be a correlation of Kd_{SrF} with metamorphic grade.

4) The overall strontium distribution coefficient is near one, indicating that there is little preference,

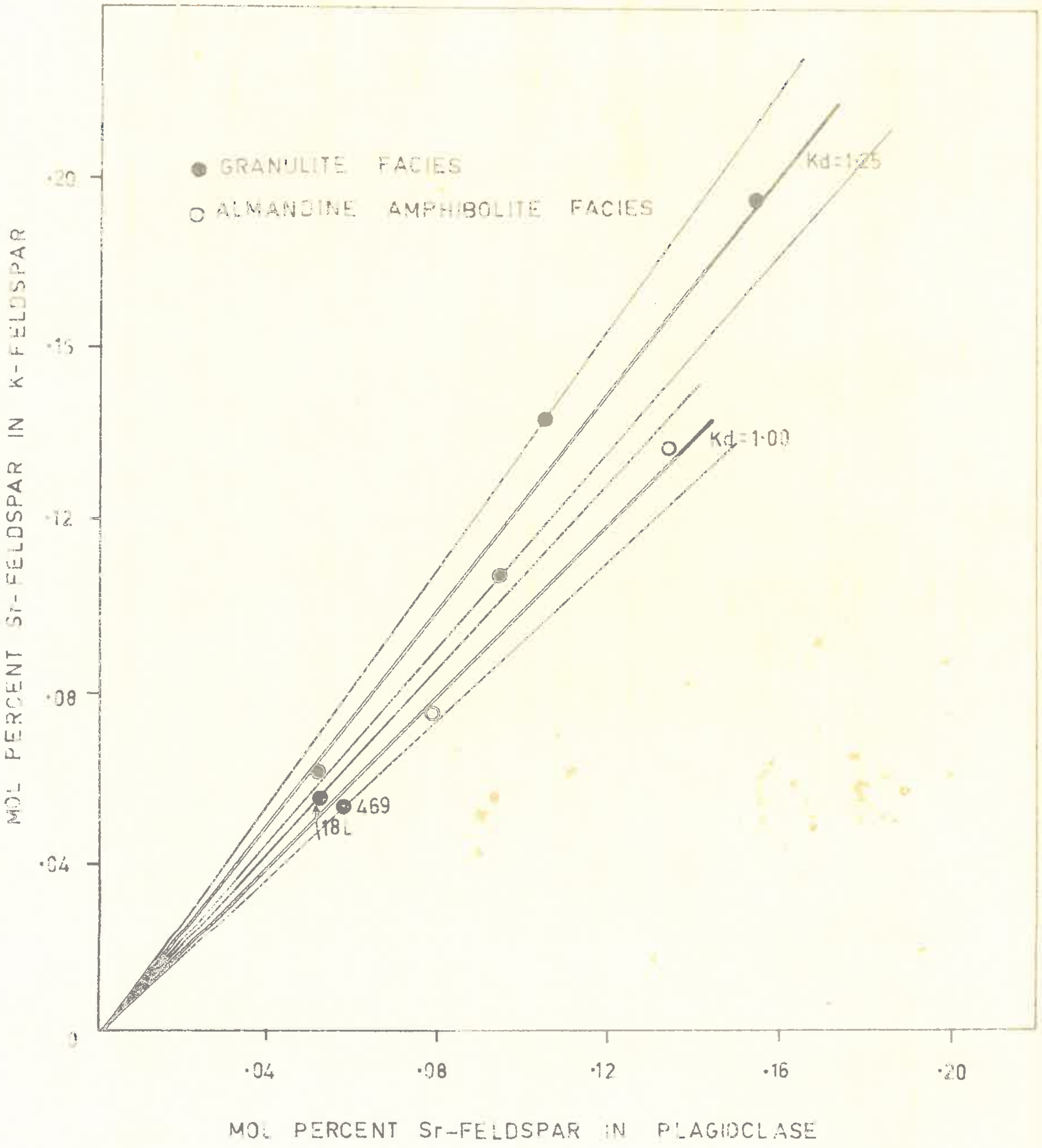


FIG. 3. DISTRIBUTION OF STRONTIUM FELDSPAR BETWEEN K-FELDSPAR AND PLAGIOCLASE

BROKEN HILL AREA

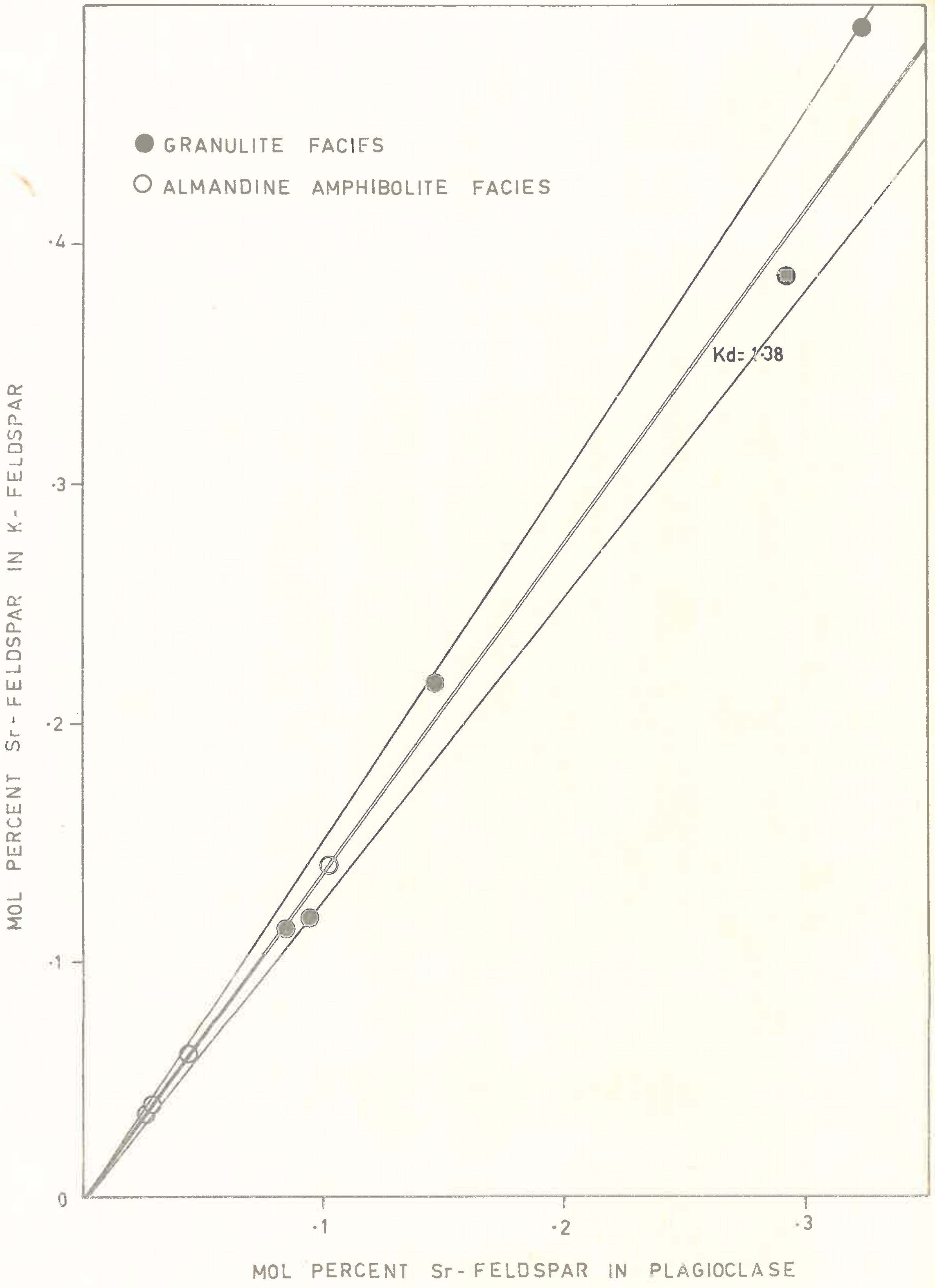


FIG. 4. DISTRIBUTION OF STRONTIUM FELDSPAR BETWEEN K FELDSPAR AND PLAGIOCLASE

CEYLON AREA

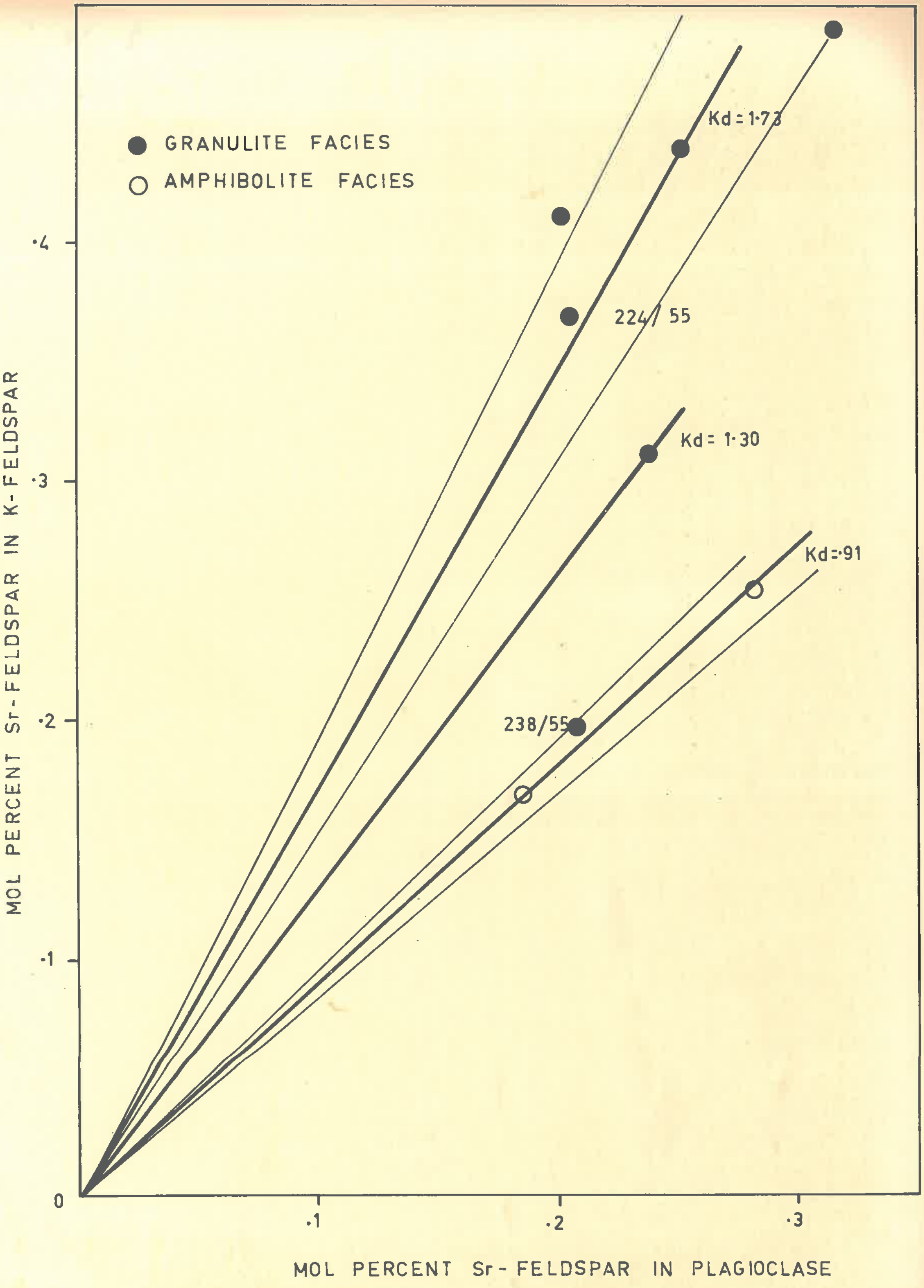


FIG. 5. DISTRIBUTION OF STRONTIUM FELDSPAR BETWEEN K-FELDSPAR AND PLAGIOCLASE LANGÖY AREA

Fig. 6 from Virgo (1966).

Distribution of Strontium felspar
between K-felspar and plagioclase
Musgrave Range Area.

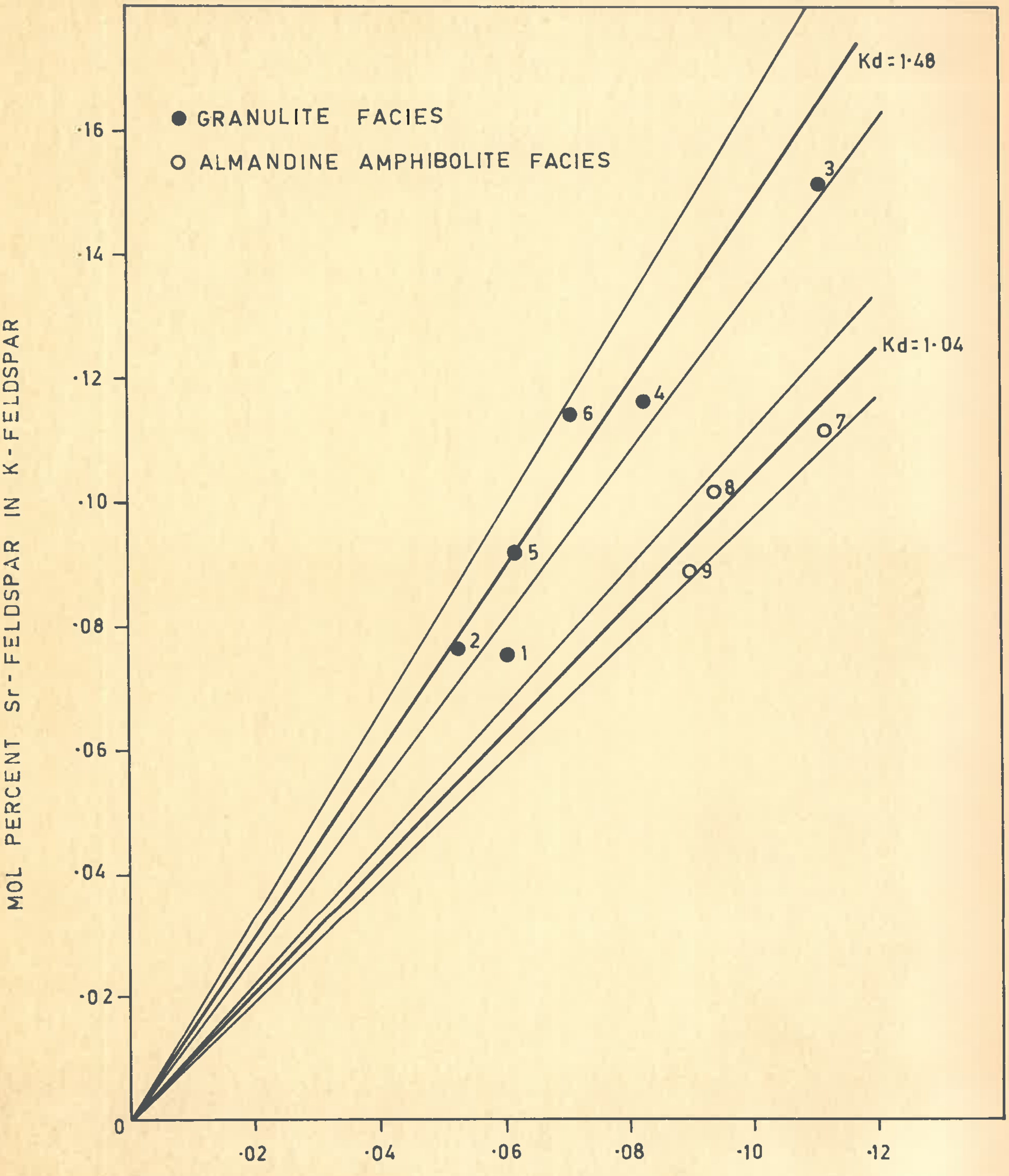


FIG. 6. MOL PERCENT Sr-FELDSPAR IN PLAGIOCLASE

on the part of strontium, for either the alkali or plagioclase felspar lattice.

Samples 1, 18L, 469 and 238/55 do not fit the above generalized features, but for each of them a special feature was reported. Sample 1 although consistent mineralogically with the highest grade of metamorphism, displayed a broad diffuse hump in the $131/1\bar{3}1$ region of the powder pattern. This is in contrast to

i) the $131/1\bar{3}1$ region of the granulite felspars, which showed a single peak in the $131/1\bar{3}1$ region,

and ii) the amphibolite facies felspars, which have triclinicities of 0.76 - 0.96.

Sample 18L occurs within a lode horizon and has fractured and sericitized grains, which in light of Binns' (1963) work suggests a later period of metamorphism.

Sample 469 was thought to be of igneous origin because of field relationships. Binns (1964) suggested that the body from which 469 was taken may not have completely recrystallized during the metamorphism which affected the surrounding rocks.

Sample 238/55 shows retrogressive effects and Heier (1960) suggested these may be the reason for its low Sr value.

In the case of the Ceylon felspars it can be seen that distribution coefficients for strontium are essentially the same for both the granulite and amphibolite materials. Virgo believed this was due to uniform metamorphism at granulite temperatures, but as a result of different bulk-rock compositions different mineral assemblages developed.

Kd_{SrF} values measured on felspars extracted from the sillimanite-muscovite and sillimanite-orthoclase sub-facies of the almandine amphibolite facies rocks occurring near Adelaide display similar properties to those indicated in generalizations 1) - 4) above.

The work of Virgo provides good evidence for a correlation of metamorphic grade with the distribution of strontium between the alkali felspar and plagioclase felspar lattices. Virgo concluded that this correlation came about as a result of the temperature variation implied by varying metamorphic grade.

This leads to the specific hypothesis that:- with increasing temperature of formation the potassium-rich felspar lattice accepts larger amounts of strontium than does the coexisting plagioclase lattice. The following chapters are concerned not only with this hypothesis but also with a similar hypothesis relating to sodium.

CHAPTER II

COMPARISON OF THE FELSPAR GEOTHERMOMETER WITH SEVERAL OTHER GEOTHERMOMETERS

Introduction

As a starting point in the study of felspar geothermometry, data given by this system was compared with temperature data deduced from coexisting mineral systems for which experimental data was available. For this purpose the following coexisting mineral systems have been compared:-

1) Alkali-felspar-plagioclase: muscovite-paragonite.
2) Alkali-felspar-plagioclase: sphalerite-pyrrhotite.

This chapter gives results of the above comparisons as well as giving detailed descriptions of the X-ray spectrographic methods which have been used in obtaining the data, on both natural felspars and the synthetic systems discussed later.

I Alkali Felspar-plagioclase: muscovite-paragonite relationships.

(a) The Micas

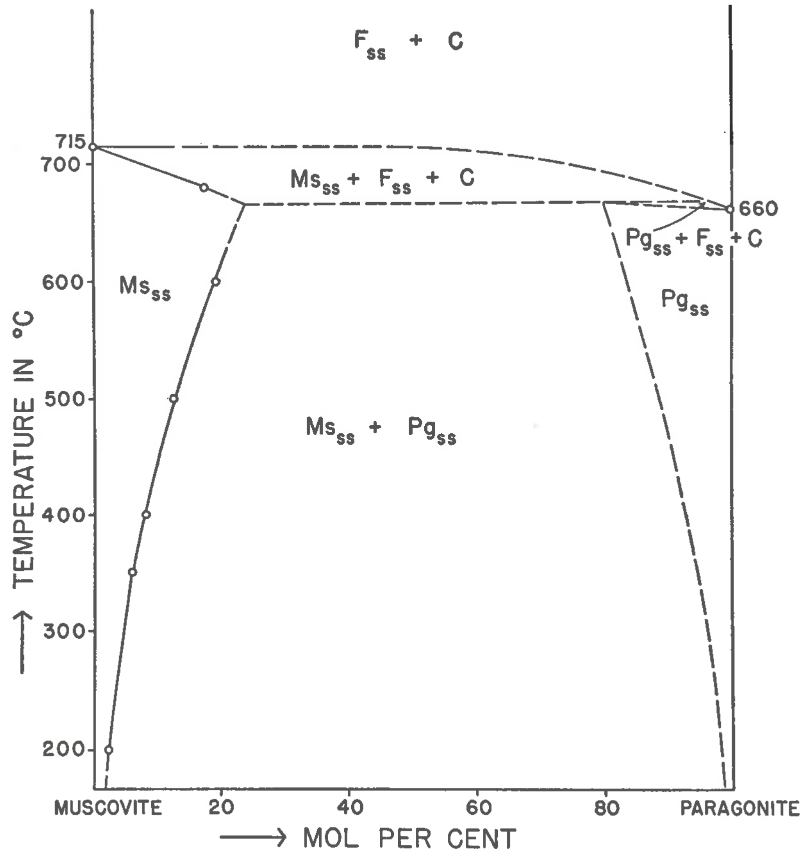
Eugster and Yoder (1955) experimentally determined the limits of solid solution of paragonite in muscovite at various temperatures and a pressure of 30,000 p.s.i.

They determined the amount of paragonite in solid solution in the muscovite, at a given temperature, by measuring the 006 spacing and assuming a straight-line relationship between C_o and composition. Their results were given in a phase diagram for the subsolidus region of the muscovite-paragonite join, Fig.7. In order to study the mica felspar relationships a series of seven granites, each containing two optically unzoned felspars and a white mica were selected. The felspars and micas were separated and purified by standard heavy-liquid and magnetic separations, with additional hand picking to ensure the mica samples were as clean as possible. For all micas both the 006 and the 0010 spacings were measured on a Philips X-ray powder diffractometer (Co/Fe radiation). Silicon powder served as an internal standard. The 111 line was used as a reference line for the mica 006 line and the 220 line as a reference for the 0010 mica line. The C_o values were then obtained by using the relationship $C_o = d001/\mathrm{Sin}\beta$, and the β value of 95°11′, given in Eugster and Yoder's paper (op.cit.). (Paragonite has a slightly smaller β value but since the amount in solid solution in the muscovite is very small the β value for muscovite has been used in these calculations).

In addition to the X-ray measurements, Na_2O and

Fig. 7.

Phase diagram for the subsolidus region of the muscovite-paragonite join, after Eugster and Yoder, 1955.



F_{ss} + C
715
700
Ms_{ss} + F_{ss} + C
660
Pg_{ss} + F_{ss} + C
600
Ms_{ss}
Pg_{ss}
500
Ms_{ss} + Pg_{ss}
400
300
200
TEMPERATURE IN °C
MUSCOVITE
20
40
60
80
PARAGONITE
MOL PER CENT

FIG. 7.

Granite Samples	Muscovite (calculated from % K_2O)	Paragonite (calculated from % Na_2O)	Co(A°)		Average Co(A°)	Temp. calculated from Micas
			from 006 spacing	from 0010 spacing		
Bodmin Moor (U.K.)	87.28 wt% 92.02 mol%	7.27 wt% 7.98 mol%	20.0712	20.0077	20.0394	400°C
Giant's Head (South Aust.)	92.68 wt% 92.28 mol%	7.47 wt% 7.72 mol%	20.0959	20.0602	20.0780	380°C
Concord (New Hampshire)	94.00 wt% 94.05 mol%	5.71 wt% 5.95 mol%	20.0502	20.0451	20.0476	345°C
Foxdale (Isle of Man)	85.97 wt% 96.16 mol%	3.29 wt% 3.84 mol%	20.0830	n.d		260°C
Binberrie Hill (South Aust.)	92.18 wt% 93.72 mol%	5.93 wt% 6.28 mol%	20.0477	20.0500	20.0528	350°C
Plumbago (South Aust.)	92.98 wt% 93.33 mol%	6.37 wt% 6.67 mol%	20.0773	n.d		360°C
Papps (South Aust.)	91.21 wt% 94.75 mol%	4.85 wt% 5.25 mol%	20.0441	20.0621	20.0531	320°C
data from E.W. Radoslovich	92.22 wt% 94.22 mol%	5.43 wt% 5.78 mol%	20.097 *			
"	15.64 wt% 15.10 mol%	84.36 wt% 84.90 mol%	19.292 ‡			
"	65.93 wt% 64.99 mol%	34.07 wt% 35.01 mol%	19.815 ‡			
"	100 wt%	-	20.090 *			
"		100 wt%	19.285 *			

Table 3 Summary of data on muscovites extracted from two felspar granites, plus data from E.W. Radoslovich.

* E.W. Radoslovich (1960).

‡ E.W. Radoslovich (personal communication and 1964 publication)

K_2O values, for each sample, were measured flame photometrically. Table 3 presents a summary of the chemical and X-ray work upon the white micas coexisting with the felspars. Included in the table is data from E.W. Radoslovich, who has made measurements upon micas of unusual compositions. Fig. 8 is a plot of the data presented in Table 3.

Examination of Fig. 8 reveals certain discrepancies between the compositions predicted by the Co values and the values determined chemically. The discrepancies are believed to arise in the following ways:-

i) presence of components such as margarite ($Ca\ Al_2\ Si_2\ O_{10}\ [OH]_2$), phengite, defined by Ernst (1963) as $K(Mg, Fe^{2+})_5\ Al_{1.5}\ Si_{3.5}\ Al_{0.5}\ O_{10}\ (OH)_2$, and varying Fe^{2+}, Fe^{3+}, Mg and Ti contents.

ii) nonlinearity of change in cell dimension with composition. Burnham and Radoslovich (1964) reported that the variation of the average alkali-oxygen distance with composition for the white micas was not linear, Fig. 9. The implication of this is that only very minor structural differences at the muscovite-rich end (actually between Mu_{86} and Mu_{100}) will be caused by the substitution of Na for K hence Co is expected to vary little in this composition range.‡

‡See Appendix IV.

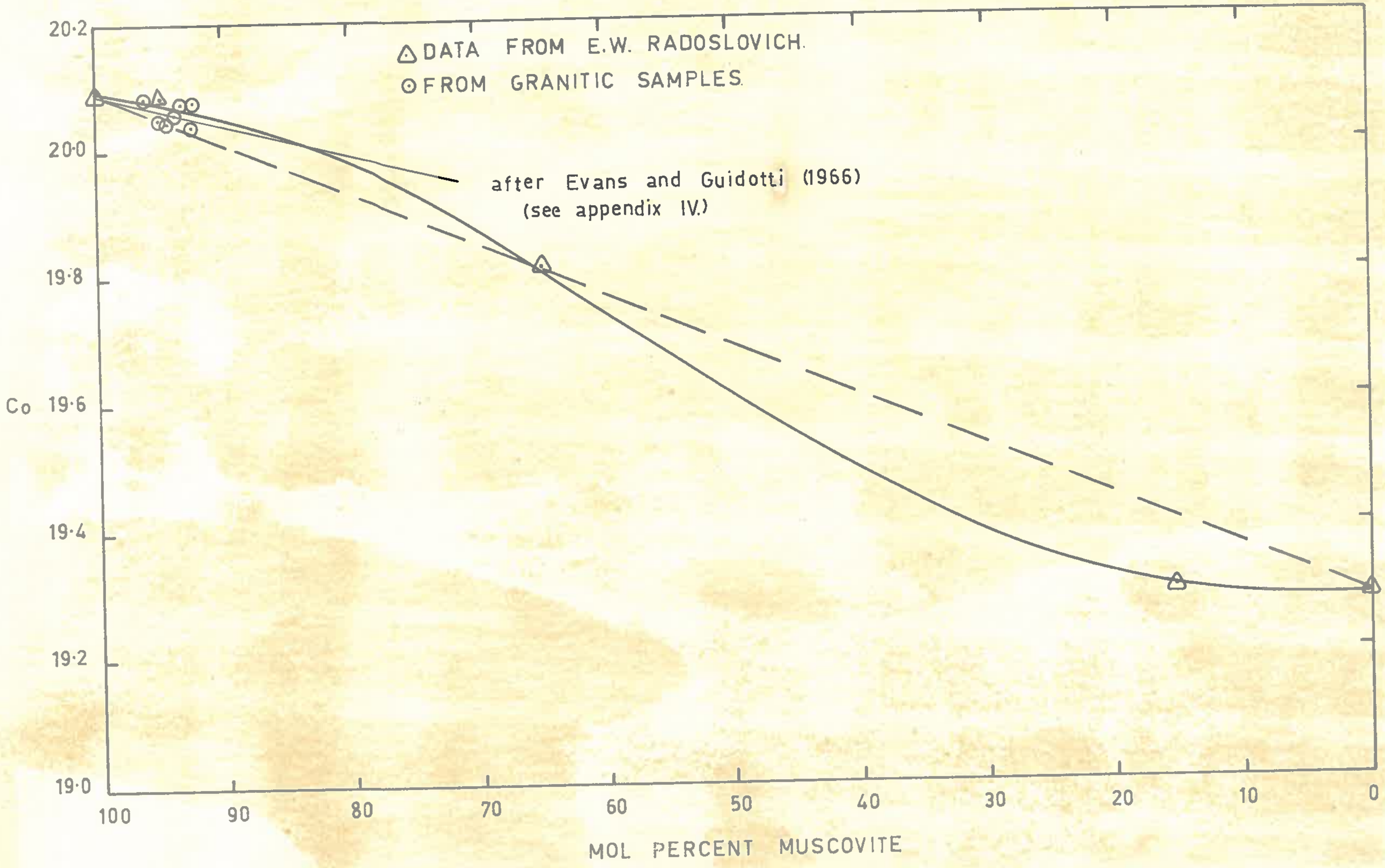


FIG. 8. PLOT Co VALUES VS. COMPOSITION FOR MICAS FROM GRANITES, PLUS DATA ON SEVERAL SAMPLES WITH UNUSUAL COMPOSITIONS.

Fig. 9. Effect of Na-K atomic substitution on average six-coordinated alkali-oxygen interatomic distances. The straight dashed line emphasizes the nonlinearity of the change of average distance with composition. After Burnham and Radoslovich, 1964.

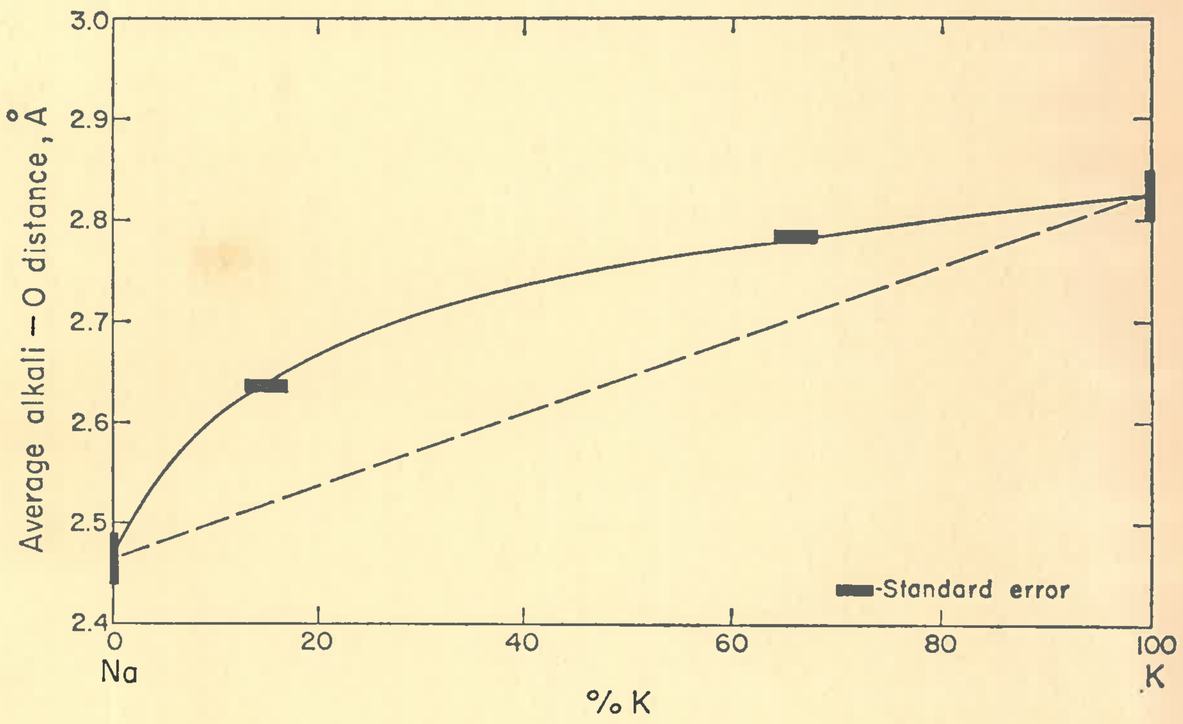

Average alkali — O distance, Å
3.0
2.9
2.8
2.7
2.6
2.5
2.4
0
Na
20
40
60
80
100
K
% K
-Standard error

FIG. 9.

As will be discussed in more detail later both gneissic and magmatic granites are represented by the material examined. Mica temperatures for the gneissic granites, Binberrie Hill, Papps and Plumbago are perhaps not too unrealistic, but rather lower than would be generally accepted. However, temperatures for the massive and presumed magmatic granites are definitely lower than expected, suggesting either the micas crystallized late in the cooling history, or they are undersaturated with respect to Na. The first suggestion can perhaps be discounted, as the micas in all specimens are not interstitial but have grain sizes comparable with those of other minerals present; strongly indicating primary crystallization. E-An-Zen and Albee (1964) found the basal spacings of coexisting muscovites and paragonites reflected metamorphic grade of the schists in which they occurred. They have suggested that muscovite can only be used as a geothermometer in the presence of free paragonite - to guarantee that the muscovite lattice will be saturated with Na at a given temperature. In felspathic rocks, such as granites, under-saturation may come about as a result of competition for sodium by coexisting felspars.

(b) The Felspars

In order to calculate Barth's variable,

$$\frac{\text{Mol fraction felspar component A in alkali felspar}}{\text{Mol fraction felspar component A in plagioclase}},$$

it was necessary to determine the elements Na, Ca, Sr, K and Rb for the coexisting alkali and plagioclase felspars. This was done upon those felspars extracted from the muscovite-containing granites and in addition upon felspars extracted from a coarse even grained granite (Wirrega), a norite, and several high grade metamorphic gneisses (Granulite (18L), and middle amphibolite facies gneisses (Rathjen, and A_{200}/879-1)).

<u>Determination of the elements listed above</u>:

i) <u>Sodium and Potassium</u> These were determined upon an EEL flamephotometer.

ii) <u>Strontium</u> This element was determined by X-ray fluorescent spectrography. The Philips spectrograph used was standard except for an attachment, fitted in front of the scintillation detector entrance collimator (Fig. 10). This attachment, designed by Dr. K. Norrish (C.S.I.R.O. Division of Soils), enables mass absorption coefficients to be measured directly.

It is known that absorption of the primary beam within the specimen and absorption of the resultant fluorescent radiation during its passage through the specimen lead to mutual absorption and enhancement effects

Fig. 10. The attachment to hold samples in the secondary X-ray beam, during direct measurement of mass absorption coefficients, is shown fitted in front of the scintillation counter entrance collimator.

Figs. 11 and 12. Jig used to press samples into perspex slide. In order that the sample mass per unit area can be calculated accurately all components are precision fitted.

FIG. 11.

FIG. 12.

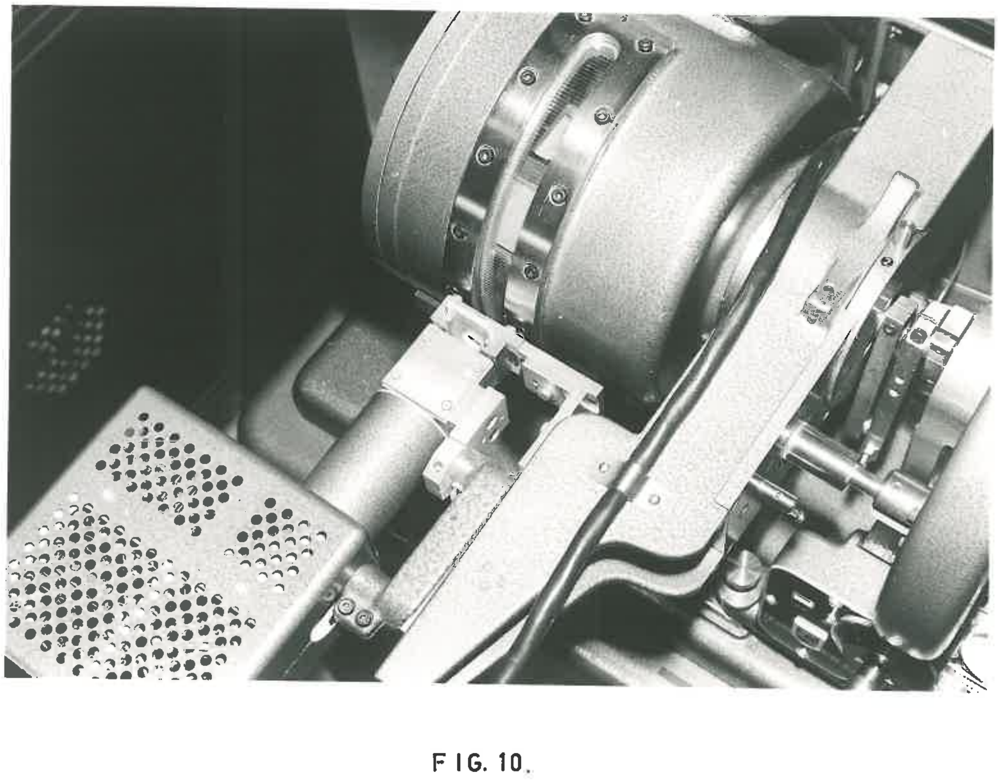


FIG. 10.

which give rise to errors in the analysis, if the composition of the standards and samples is different. A knowledge of the mass absorption coefficients for the standard and samples, at the wavelength of the element being determined, enables matrix differences between standard and sample to be allowed for.

Measurement of mass absorption coefficients was based upon the following considerations. When a parallel beam of monochromatic X-rays with an incident intensity I_o passes through a plane parallel layer of material of thickness t cms. with surfaces normal to the beam and more than covering the total beam cross section, the emergent intensity I is given by:-

$I = I_o e^{-\mu t}$, where μ is the linear absorption coefficient. The reduction in intensity of the primary beam is determined by the quantity of matter traversed by the beam, hence a mass absorption coefficient can be defined as

$\mu_m = \mu/\rho$, where ρ is the density.

μ_m is, to a good approximation, independent of the physical state of the material.

$$I = I_o\, e^{-\mu/\rho . t\rho}$$

$$\therefore \quad \ln I = \ln I_o - \mu/\rho . t\rho$$

$$\therefore \quad \ln I_o/I = \mu/\rho . t\rho \text{ (cm}'\times\text{mass}\times\text{cm}^{-3}$$

$$= \text{mass/cm}^2 \text{ which are the units for } t\rho).$$

$$\therefore \quad \mu/\rho = \mu_m = \frac{\ln I_o/I}{\text{mass/cm}^2}$$

μ_m can therefore be determined at a given wavelength if the quantities I_o/I and the mass/unit area of the sample in the X-ray beam can be measured.

In practice the mass per square centimeter was found by first weighing a perspex slide, which had cut into it an accurately machined hole (area 1.252 sq. cms.). Into this was pressed, with the jig illustrated in Figs. 11 and 12, about 0.5 gm of sample powder.

After reweighing the slide, with the sample tablet included, the sample mass per unit area could be calculated. The values of I_o/I were obtained, for SrKα_1 radiation, by irradiating a disc of $SrCO_3$ with X-rays from a Mo tube powered such that a fluorescent intensity of 50,000 c.p.s. was obtained when the plastic slides containing the felspar tablets were out of the beam. The exact value of I_o was obtained by measuring the times necessary to accumulate 10 × 40,000 counts and then applying a "dead-time" correction. The values of I were found in a similar way after the perspex slides, and samples, had been fitted into the attachment on the goniometer arm. (Fig.10).

Strontium values for the felspar unknowns could then be calculated from:-

$$\text{Sr content of unknown} = \text{Sr content of standard} \times \frac{\mu_m \text{ unknown}}{\mu_m \text{ standard}} \times \frac{\text{X c.p.s.}}{\text{Std. c.p.s.}},$$

where μ_m unknown and μ_m standard are the mass absorption coefficients, at the SrKα_1 wavelength, for unknown and standard respectively. The line intensities for the unknown and standard are represented as X c.p.s. and Std. c.p.s..

G$_1$ proved to be a suitable standard for the Sr analyses. By comparing it with W$_1$ and two adamellites, on which isotope dilution values for Sr had been obtained by W. Compston of the Australian National University (pers. comm. S. Shaw 1963) a figure of 257 ppm for Sr in G$_1$ was arrived at. This agrees well with the value 250 ppm quoted by Ahrens and Fleischer (1960).

The preparation for analysis of samples in the form of tablets comprising a half of a gram of sample powder backed by boric acid, followed the method of Baird (1961), except that an aluminium sleeve with an I.D. of 1.57 cm (instead of the 2.8 cm recommended by Baird for full size samples) was used in the sample forming die.

(iii) Calcium

Calcium was determined by EDTA titrations using Acid Alizarin Black as an indicator. Interference by Group III elements was prevented by complexing with Triethanolamine. End points were precisely detected by using an EEL photometric titrator. The accuracy of this method was checked by comparison of the result on a standard felspar with those obtained by other methods.

(iv) Rubidium

The Rubidium values for the granite felspars were measured on the X-ray spectrograph. Once the mass absorption coefficients had been measured for the $\mathrm{SrK}\alpha_1$ wavelength, coefficients at the $\mathrm{RbK}\alpha_1$ wavelength were obtained from the relationship

$$\frac{\mu_m \mathrm{RbK}\alpha_1}{\mu_m \mathrm{SrK}\alpha_1} = \frac{(\lambda\ \mathrm{RbK}\alpha_1)^3}{(\lambda\ \mathrm{SrK}\alpha_1)^3} \quad \text{which}$$

is valid so long as an absorption edge does not come between the two wavelength values concerned (Henry, Lipson and Wooster 1961). Calculation of the Rubidium values on the unknowns followed the same method as that used for Sr. G_I was used as a standard, a value of 216 ppm Rb was chosen.

Calculation of Felspar Components and Distribution Coefficients

After the determined weight percentage oxides had been converted to the appropriate felspar components these were retotalled to 100%. Retotalling was required chiefly for those plagioclases containing quartz (which in no case represented more than 8% of the sample). The adjusted weight percentages were then converted to molecular percentages from which were calculated Kd_{Ab}, K_{dSrf}, and $K_d An$ thus:-

$$Kd_{Ab} = \frac{\text{Mol\% Ab in Alkali Felspar}}{\text{Mol\% Ab in Plagioclase Felspar}}$$

$$K_{dSrf} = \frac{\text{Mol\% Srf in Alkali Felspar}}{\text{Mol\% Srf in Plagioclase Felspar}}$$

$$K_d An = \frac{\text{Mol\% An in Alkali Felspar}}{\text{Mol\% An in Plagioclase Felspar}}$$

(c) Results from both Micas and Felspars

Table 4 sets out the results for the felspars extracted from the seven muscovite containing granites and also for the five other rocks mentioned earlier. Temperatures deduced from these felspars are compared with those from the corresponding micas. Inspection of the table reveals that 1. Only in the case of the gneissic granites Binberrie Hill, Papps and Plumbago is there any coincidence between temperatures deduced from Barth's (1956) graph, of temperature versus distribution coefficient for albite, and the mica temperature. The agreement between the muscovite and felspar temperatures for the three samples mentioned is very likely fortuitous, since

i) the muscovites may be undersaturated with Na,

ii) the temperature values assigned by Barth to given distribution coefficients for albite were empirical.

iii) the subsolidus region of the muscovite-paragonite join (Fig.7) was based upon compositions obtained from the variation of Co with paragonite content assuming a straight line between Co paragonite and Co muscovite. The work of Burnham and Radoslovich (op.cit.)

Sample	Rock Type	Alkali Felspar Components (Mol%)					Plagioclase Components (Mol%)					Distribution Coefficients			Temp. from Kd_{Ab}	Temp. from Micas
		Ab	Or	An	Srf	Rbf	Ab	Or	An	Srf	Rbf	Kd_{Ab}	Kd_{Srf}	Kd_{An}		
Wirrega South Aust.	Granite	41.99	56.54	1.248	.0051	.2271	87.08	6.698	6.184	.0079	.0282	.482	.648	.202		
Bodmin Moor (U.K.)	Granite	33.76	63.44	2.532	.0630	.213	85.50	3.55	10.89	.0463	.0001	.395	1.361	.233	650°C	400°C
Giant's Head South Aust.	Granite	25.18	73.32	1.170	.0072	.3269	94.03	2.291	3.675	.0033	.0039	.268	.221	.319	525°C	380°C
Concord New Hampshire	Granite	11.48	87.44	0.8012	.0496	.2275	82.67	6.899	10.39	.0259	.0207	.139	1.925	.077	400°C	345°C
Foxdale Isle of Man	Granite	12.51	86.37	0.743	.0547	-	90.08	1.840	8.057	.0282	-	.139	1.939	.092	400°C	260°C
Binberrie Hill South Aust.	Gneissic Granite	10.40	88.51	0.762	.0149	.3117	89.02	6.415	4.536	.0089	.0020	.116	1.674	.168	375°C	350°C
Plumbago South Aust.	Gneissic Granite	10.86	88.20	0.584	.0146	.3377	95.14	2.616	2.238	.0033	.0098	.114	4.421	.261	370°C	360°C
Papps South Aust.	Gneissic Granite	6.71	92.43	0.546	.0338	.2895	97.14	1.135	1.711	.0114	.0074	.069	2.968	.319	330°C	320°C
Broken Hill 18L	Granulite-Amphibolite Gneiss	9.65	89.46	0.603	.0539	.2357	6.622	2.458	90.86	.0476	.0172	1.457	1.132	.007		
Norite Black Hill South Aust.	Norite	14.52	81.69	2.923	.2680	-	45.18	2.488	52.06	.2660	-	.321	1.008	.056		
Rathjen South Aust.	Gneiss	9.34	89.46	.344	.0608	-	78.54	1.82	19.56	.0807	-	.119	0.753	.018		
A_{200}/879-1	Gneiss	5.60	93.63	.268	.0159	-	87.11	2.556	10.28	.0222	-	.064	.717	.026		

Table 4 Data obtained on felspars and micas from granites. Also shown are distribution coefficients for felspar constituents of felspars from granites and gneisses not containing white mica.

suggests this correlation will not be strictly valid, even for very potassium rich samples.

2. Although the distribution coefficients for albite, for the granites, have been arranged in order of decreasing values the coefficients for strontium felspar and for anorthite do not follow in the same sequence.

3. For the granites Giant's Head, Bodmin Moor and Wirrega, not only are the Kd_{Ab} values high, but also the albite contents of the alkali felspars are high; leading us to expect, both from the Barth albite geothermometer and from solvus relationships, higher temperatures of equilibrium for these samples than for the others. The results for these granites do not confirm, in any simple way, Barth's hypothesis that distribution coefficients for anorthite and strontium felspar increase with temperature.

(d) The Validity of the Barth Geothermometer in Relation to Plutonic and Metamorphic Rocks.

Granites cool in the presence of water which will aid transfer reactions tending to adjust compositions of minerals already crystallized towards values appropriate to the prevailing temperature and pressure conditions. The extent to which these transfer reactions can take place will depend upon the ease with which elements migrate along intergranular boundaries and through individual mineral lattices. The effect of these hydrothermal transfer reactions will be to vary the compositions of parts of the crystals formed at higher temperatures. The net result will make measured compositions of individual minerals not representative of any one temperature.

On the other hand, metamorphic rocks have preserved in them equilibrium assemblages of minerals not stable under normal temperature and pressure conditions. This implies that after the culmination of a metamorphic cycle, processes are operative which prevent the high temperature assemblage changing in response to falling temperature and pressure.

Before the waning of a metamorphic cycle, water is either locked up in hydrous minerals or lost, hence it is not available to "flux" retrograde reactions. As it is likely that water plays an important part in the partitioning of elements in sympathy with a set of superimposed conditions, loss of this water will mean information concerning high temperature equilibrium states will be preserved.

On the basis of these considerations it seems not unreasonable to expect metamorphic rocks to develop equilibrium assemblages of minerals with compositions reflecting superimposed conditions.

As has been shown in the last chapter, data from high grade metamorphic rocks is more consistent with Barth's hypothesis than the data from granites.

II Alkali felspar-plagioclase: sphalerite-pyrrhotite relationships.

By determining the amount of FeS which goes into solid solution in ZnS at various temperatures Kullerud (1953) was able to develop the FeS-ZnS system as a geothermometer. The effect of FeS solid solution at any one temperature was indirectly found by measuring the cell edge of sphalerite. Skinner, Barton and Kullerud (1959) found Kullerud's original spacing curve to be in error since oxygen had entered the sphalerite structure causing a reduction in cell volume and they corrected this fault.

Since the sphalerite geothermometer is based upon accurate experimental work, a valid comparison of geothermometric results from the sulphides, with those from felspars taken from the same immediate environment should be significant.

The material studied was taken from across a contact between the zinc lode and the enclosing sillimanite garnet gneiss from the eighteenth level at the Zinc Corporation's Main Mine at Broken Hill. Since the ore sample, which contained free pyrrhotite, was taken from within 2 feet of the gneiss sample temperatures were likely to have been comparable in each material.

(a) <u>The Sulphides</u>

After a clean sample of sphalerite had been obtained by magnetic separation, the cell edge was measured by comparing the position of the ZnS(111) line with the (200) line of analytical grade sodium chloride for which, at 25°C, Dr. J.B. Jones had obtained an a_o value of 5.6402 ± .0004A°. The d_{200}, at 20°C, was computed as 2.8196 (using a $\Delta C_o/^{\circ}C = 227 \times 10^{-6}$). ~~Thus~~ This corresponds to a 2θ value of 31.735° for ~~CaKa~~ CuKα radiation. On the basis of six diffractometer oscillations over the (111) peak of ZnS and the (200) line of NaCl, an a_o value of 5.4223A°, for the sphalerite sample 18L, was obtained. The following formula given by Skinner et. al. (op. cit.) enabled the composition of the Broken Hill sample to be ~~measured~~ calculated:-

$a_o = 5.4093 + 0.000456X$, where a_o is the unit cell edge of a sphalerite containing X mol percent FeS. Substitution of the measured a_o value into this formula indicates the Broken Hill sample contains 28.15% FeS. From Fig. 13 we can derive an equilibrium temperature of 685°C which compares favourably with the value >600°C quoted by Edwards (1956) for the Broken Hill sphalerites.

This value should be regarded as a minimum, since Skinner's work indicated that Kullerud's solvus should be raised, in addition there is a positive correction for pressure which Kullerud estimated at 25°C/1000 bars. (Segnit (1961) tentatively accepted a pressure of the order of 3000 bars for the Broken Hill lode). Manganese, cadmium and copper have an effect on the sphalerite-pyrrhotite equilibrium relationship, but as these elements are present only in small amounts in the sphalerite they have little effect upon the temperature estimate. See Kullerud (1953); Skinner (1959) and Toulmin (1960).

(b) <u>The Felspars</u>

These were taken from the wall rock Granulite Facies gneiss which had as its mineral assemblage:- Almandine rich garnet, sillimanite, anorthite (An_{90}), potassium felspar (orthoclase), quartz, biotite and

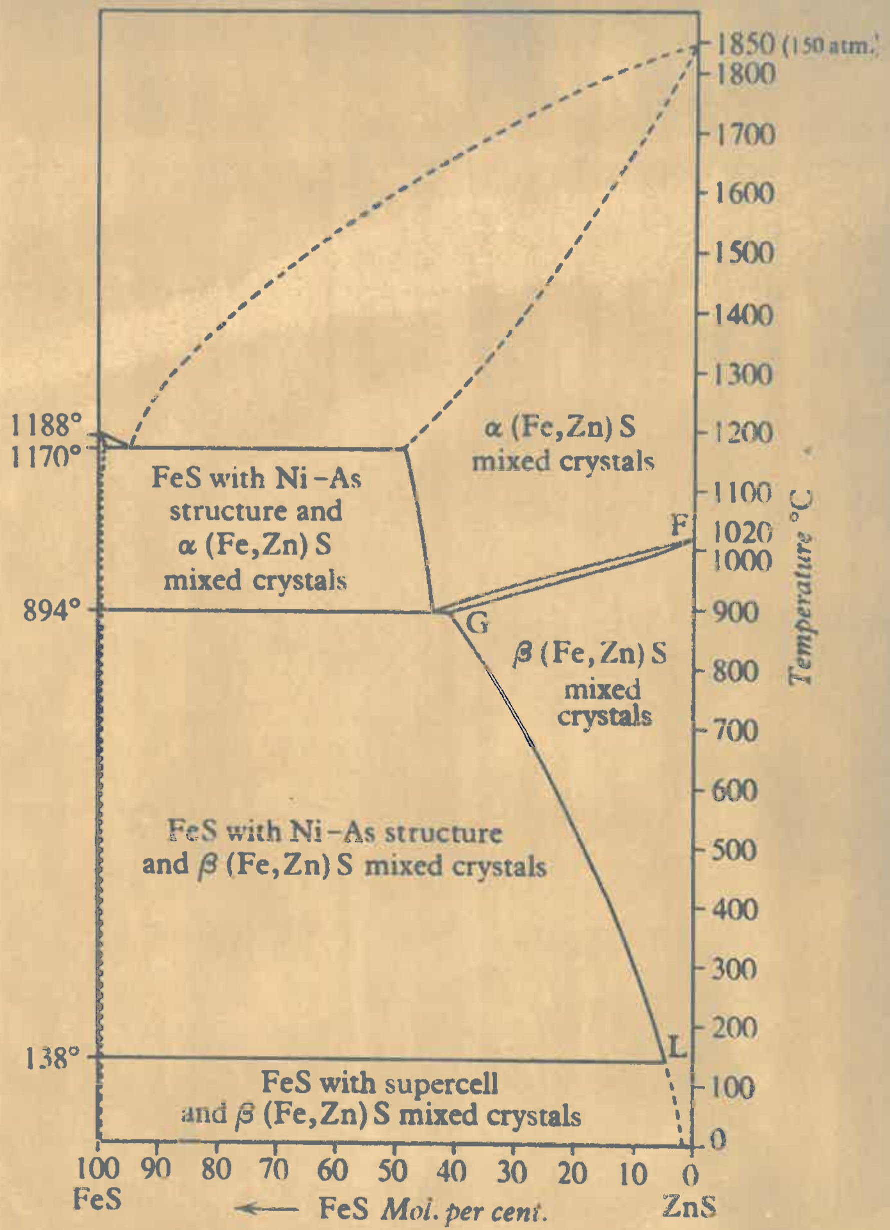


FIG. 13. Phase relations in the system FeS–ZnS (after Kullerud, 1953).

Component	Plagioclase	Alkali Felspar	Distribution Coefficients
Or	2.458	89.46	$Kd_{Ab} = 1.457$
Ab	6.622	9.65	$Kd_{SrF} = 1.132$
An	90.860	0.60	$Kd_{An} = 0.007$
Srf	0.0476	0.054	
Rbf	0.0172	0.2357	

Table 5 Showing, in Mol%, the data on coexisting felspars from Broken Hill.

minor amounts of ilmenite. The analytical results on the felspars are given in Table 5. The remarkably high distribution coefficient for albite in the examined felspars from Broken Hill is clearly the result of the high anorthite content of the plagioclase. This, in turn, reflects the importance of the calcium content of the sediment undergoing metamorphism. In spite of the high calcium plagioclase the distribution coefficient for strontium felspar is near one; a reasonable value in light of data on other felspars from high grade metamorphic areas, and results of synthetic experiments (see later). In addition this value of about one for Kd_{Srf} seems to disprove any geochemical coherence between strontium and calcium.

The minimum temperature of 685°C deduced from the sphalerite suggests Heier's (1960) Kd_{Ab} temperatures, (400°-500°C) for amphibolite facies rocks, are perhaps too low.

Conclusions

The work described in this chapter shows there is little correlation between the geothermetric results obtained for the several mineral systems examined.

The systematic variation of the distribution coefficients for anorthite and strontium felspar, predicted by Barth, has not been observed for felspars from granite rocks.

It is suggested this is an expression of non equilibrium in such rocks.

Work on a potassium felspar coexisting with a very calcic plagioclase does not suggest that Sr follows Ca in its distribution mode, in fact, approximately equal amounts enter the alkali felspar and plagioclase lattices.

At the time the work reported in Chapter II was carried out the X-ray spectrograph was a new analytical tool in the Department of Geology. Therefore, not only were calibrations and suitable standards to be obtained but also tedious experiments had to be run to determine the "dead-time" of the electronics. This was a very necessary correction factor to be applied to those high counting rates obtained from the unattenuated beam used during mass absorption measurements. In addition to these fundamental calibrations the use of the spectrograph for felspar analysis required small samples; hence modifications had to be made to sample holders.

These early experiments, although time consuming, later proved invaluable in that they provided the experience to allow analytical work on synthetic felspars to proceed readily.

CHAPTER III

EXPERIMENTAL METHODS USED TO INVESTIGATE THE An-Or-Ab-H_2O-$SrCl_2$ SYSTEM

I Introduction

The second phase of the present study was a direct investigation, in artificial systems, of the behaviour of the elements K, Na, Ca and Sr when partitioning between coexisting felspars. The experimental investigations were undertaken to check the hypothesis, based on limited data for natural felspars, that Kd_{SrF} and Kd_{Ab} values reflect temperature influences. These influences, and the effects of bulk composition needed defining more clearly.

In short, not only did the partitioning behaviour of Sr need investigation, but information was also required on subsolidus relationships in the system $Ca\,Al_2\,Si_2\,O_8 - K\,Al\,Si_3\,O_8 - Na\,Al\,Si_3\,O_8 - H_2O$. Information from this system seems to be particularly relevant to an understanding of metamorphic felspars, for as Orville (1962) comments:- "it is entirely possible that a major part of the material present in crystalline phases in most regionally metamorphosed rocks has passed through a state of solution in a volatile-rich intergranular field". This chapter describes the apparatus and experimental techniques used to acquire data on the $Ca\,Al_2\,Si_2\,O_8 - K\,Al\,Si_3\,O_8 - Na\,Al\,Si_3\,O_8 - H_2O - (SrCl_2)$ system.

II The Experiments

The hydrothermal experiments to determine the compositions of coexisting alkali felspars and plagioclases were arranged as in Fig. 14.

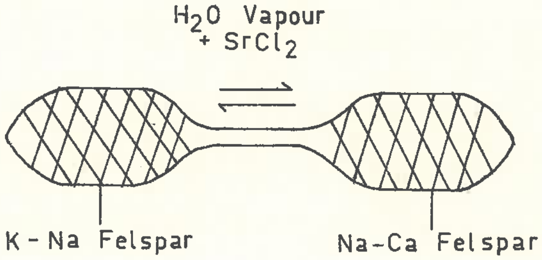


Fig. 14 Cross-section of charge in a hydrothermal experiment.

Two felspar "gels", one an alkali felspar and the other a plagioclase, each weighing 130mgms. were placed at either end of a platinum capsule together with 100mgms of $Sr\,Cl_2$ solution. The felspars were confined to the ends by crimps and the capsule sealed by welding. The idea of a reaction capsule which allows ionic diffusion, through a vapour phase, between two physically separated solid phases comes from Orville's (1963) paper in which is described an interesting experiment to test the differential migration of Na and K between alkali felspars in a temperature gradient.

(1) The Technique of Producing Capsules

This was only perfected after considerable experimentation. A platinum tube 1$\frac{7}{8}$" long, outside diameter 0.200" and with a wall thickness of 0.008" was cleaned in a hot hydrofluoric-sulphuric acid mixture. After annealing, a trifoil crimp, ¼" long, was formed in one end with a three jaw drill chuck. This crimp was then sealed by welding with a small oxy-acetylene flame. The first charge, consisting of 130mgms of felspar "gel", was introduced with the aid of a small glass funnel which prevented any of the upper inner surface of the capsule being contaminated with powder. After 0.1cc of $SrCl_2$ solution had been introduced from a micrometer syringe the lower section of the capsule was closed off with a tool designed and engineered for the purpose. This tool, which was operated by a 4" 3-jaw lathe chuck, is shown in the accompanying photograph (Figs. 15 and 16). The second charge, consisting of 130mgms of felspar "gel" was then introduced (with the aid of the glass funnel to prevent powder contaminating the weld, to be made after the second end had been crimped). To prevent liquid in the capsule evaporating during the final welding operation the capsule was frozen into ice in a thick-walled brass cup fitted with a drilled lid such that

Fig. 15. View of disassembled crimping die. The stem into which the jaw slots were milled was made in two pieces to enable capsules, which tended to jam during crimping, to be released.

Fig. 16. View of assembled crimping die and a completed reaction capsule.

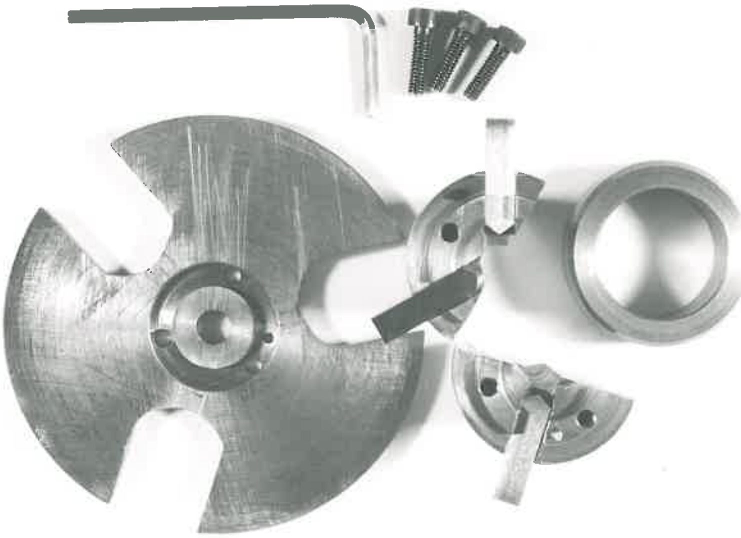


FIG. 15.

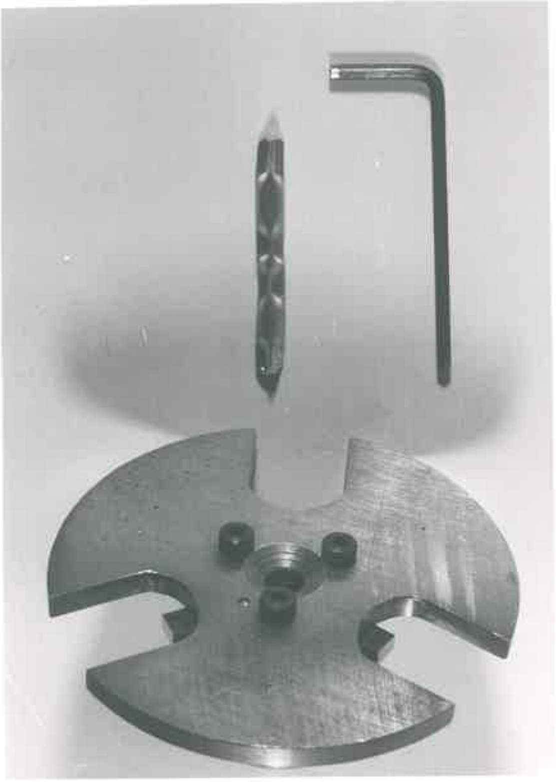


FIG. 16.

the final crimp could stand proud about 3/16". Each weld was carefully scrutinized with a microscope to detect flaws. After some experience capsules could be produced readily but even then there would be an occasional failure during an experiment, which of course had to be re-run. Leakage during an experiment was detected either by non-collapse of the capsule or failure of liquid to ooze out when the envelope was clipped at the end of a run.

(2) Preparation of Starting Materials

The synthetic starting materials used were felspar "gels" made by the methods of Roy (1956), Shaw (1963), and Luth and Ingamells (1965). "Gels" with close to the following compositions were prepared Or_{100}; Ab_{100}; Ab_{20} Or_{80}; Ab_{85} An_{15}; Ab_{70} An_{30} and Ab_{25} An_{75} (these materials were prepared at the inception of the work but other compositions were later prepared to test various hypotheses. These will be described in appropriate places).

The starting materials used were as follows:-

i) A.R. KNO_3

ii) A.R. $NaNO_3$

iii) Pure aluminium foil, which was carefully dissolved, in appropriate amounts, in 20 A.R. nitric acid (hot).

iv) "Ludox" an ammonia stabilized colloidal solution of SiO_2, obtained from E.I. Du Pont De Nemours and Co (Inc.) Industrial and Biochemicals Department, Wilmington, Delaware U.S.A. This solution was analysed, in triplicate, for SiO_2 and the following results obtained 36.13, 36.06, 35.93 giving an average silica content of 36.04% (w/V). A dehydrated portion of the Ludox was flame photometrically analysed for Na_2O and K_2O; whereas the K_2O content was quite insignificant, the Na_2O content was measured at 0.10% which accords quite well with the value 0.14% obtained by the U.S.G.S. and reported in Shaw's (1963) paper.

v) $CaCO_3$

The analytical grade chemical prepared by the British Drug Houses Ltd. was found to contain considerable quantities of strontium which had to be removed. An ion-exchange method to separate Ca and Sr proved completely suitable. The technique used, which is based upon a method by Povondra and Sulcek (1961), is described in appendix I.

To prepare the "gels", appropriate amounts of the required starting materials were added, in solution to acidic solutions of Ludox. The resulting mixtures, after careful stirring, were slowly dehydrated in platinum dishes, first on a water bath and then in an electric oven at 105°C. After dehydration the nitrates were decomposed and the ammonia driven off by heating the platinum dishes on the hearth of an electric furnace. The dried oxides were transferred to a steel "Specs" mill in which they were crushed to a size somewhere between 20 and 50 microns. The fine powders were transferred to closed platinum crucibles and heated at 700°C for one hour to expel remaining water. All samples were stored in a dessicator containing magnesium perchlorate.

A portion of each "gel" prepared was crystallized hydrothermally and the resulting high temperature product X-rayed to check for foreign phases. In all cases sharp clear patterns were obtained, free from any suggestion of foreign material. For the albite, crystallized at 850°C, 17,000p.s.i. for 65 hours, the separation between $2\theta_{131}$ and $2\theta_{131}$ (CuKα) was measured as 1.92°2θ. This value, in light of Mackenzie's (1957) work, suggests the product was not maximum high albite. The $\bar{2}01$ spacings for the albite and the sanidine prepared from the "gels" are compared in Table 6 with values for Ab_{100} and Or_{100} quoted by

Sample	Orville's $d_{\bar{2}01}$	Present values	Conditions of formation
Orville's Or_{100}	4.234	4.2345 4.2336	1 hour; 700°C 2000 bars
$Or_{98.7}$ crystallized from "gel"		4.2333 4.2343 4.2336	65 hrs; 850°C 17,000 psi.
Orville's Ab_{100}	4.0345	4.0325	1 hour; 700°C 2000 bars
Ab_{100} crystallized from "gel"		4.0344	65 hrs; 850°C 17,000 psi.

Table 6 $\bar{2}01$ spacings of albite and sanidine prepared for this work compared with Orville's 1966* data.

* Personal Communication:- see note at end of chapter.

Dr. Orville in a personal communication (1966), and with the values, obtained by the author, on samples of Ab_{100} and Or_{100} kindly supplied by Dr. Orville. The author's measurements were obtained by comparing the 2θ value of the felspar $\bar{2}01$ line with the 2θ value of the 101 line of potassium bromate. Each comparison resulted from three forward and three reverse diffractometer scans.

(3) Hydrothermal Apparatus

General views of the apparatus constructed for the experiments are shown in Figs. 17 and 18 and diagramatically illustrated in Fig. 19. Pressure was transmitted to the outside of the platinum reaction capsule by argon compressed by the intensifier I. Pressure measurement was achieved with 0-30,000p.s.i. chrome-vanadium Bourdon Tube gauges made by the National Instrument Company. These were arranged to constantly monitor the pressure in the pressure-vessel assemblies which were standard Tuttle Cold Seal Vessel model MRA-114R supplied by TEM.PRES. RESEARCH INC.

(a) The pressure intensifier, constructed in the engineering workshops at the University of Adelaide

Fig. 17. Photograph of pressure intensifier, and one of the horizontally mounted furnaces. At the right-hand end can be seen the connections to the controlling thermocouple, and at the left-hand end the air inlet to the quenching ring.

Fig. 18. Power supplies; the supply for the main winding of a single furnace is shown at the left, supplies for the smaller platinum windings, for two furnaces, are seen at the right.

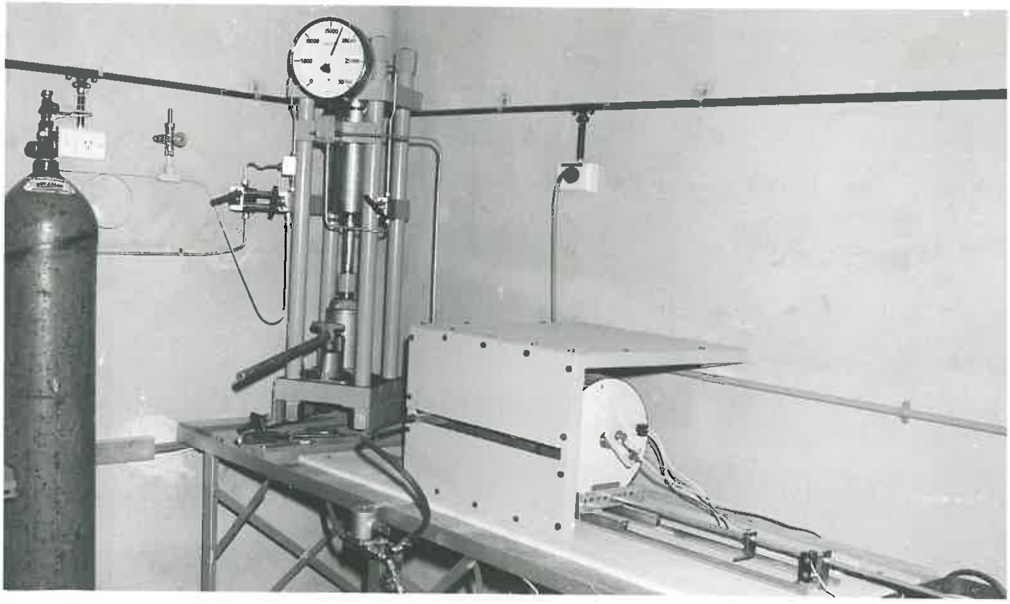


FIG. 17.

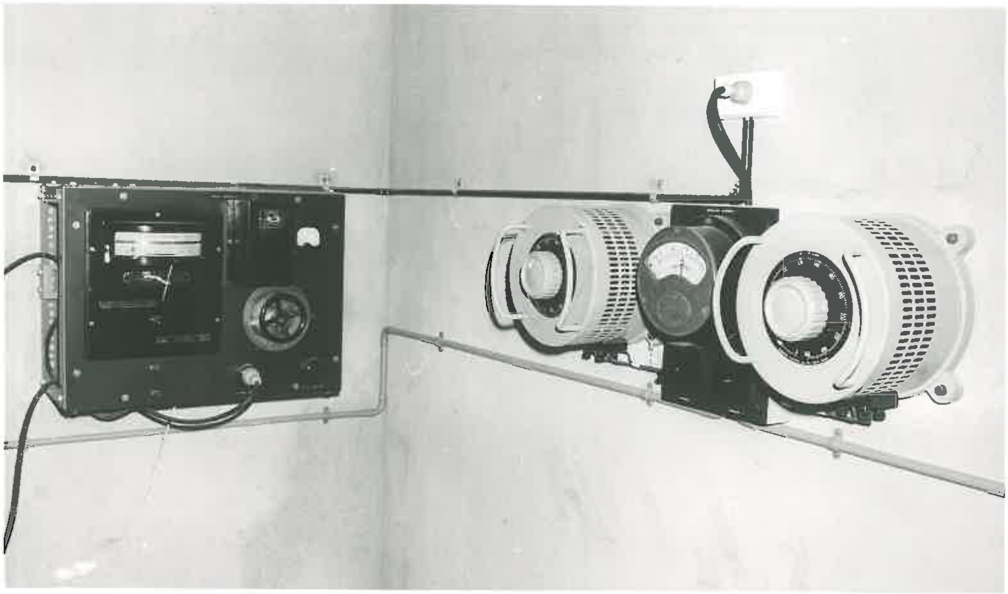


FIG. 18.

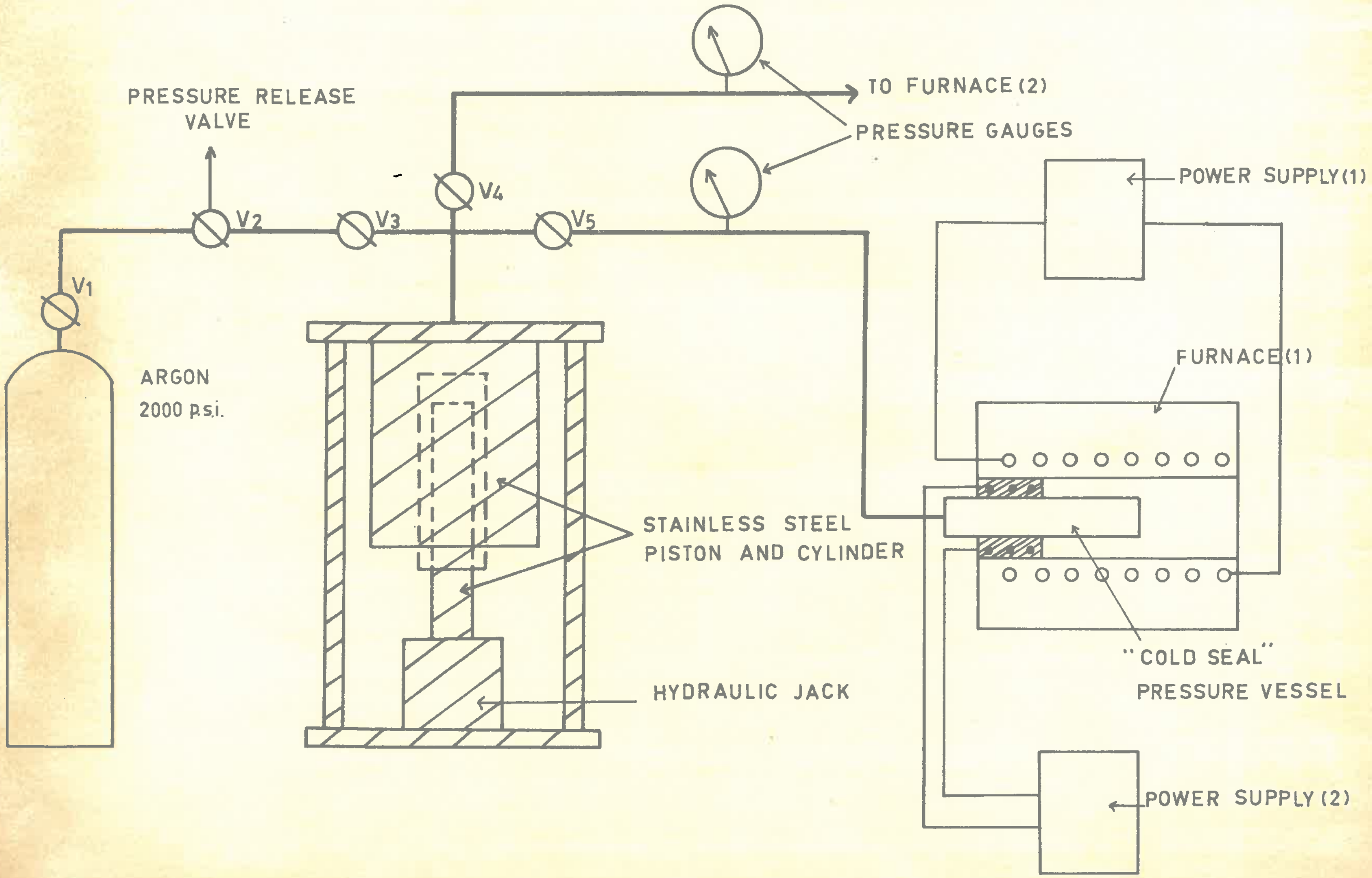


FIG. 19. SCHEMATIC LAYOUT OF HYDROTHERMAL APPARATUS.

was based upon a design suggested by M. Paterson (pers. comm.) of the Australian National University. It consists of a chrome-plated hard steel piston 1.125" diameter which passes, as shown in Fig. 20, through a seal into a thick-walled stainless steel cylinder, OD = 5", ID = 1.130", length 10.5", closed at the opposite end with a screw-in seal bearing upon an annealed copper ring. This cylinder design was decided upon as it did not require a long accurately-machined bore to be developed.

The seal between the piston and cylinder consists of a lurene O-ring compressed by a gland nut lined with a sintered lead-teflon bush and transmitting its thrust to the "O-ring" through a chrome-plated hard steel sleeve hand-lapped to match the piston. A fifteen ton hydraulic press was used to force the piston into the cylinder, the whole mechanism was mounted, as shown in Fig. 17, between accurately milled steel plates held together by four high tensile steel bolts. The hand operated inlet and outlet values were Aminco standard high pressure fittings. High pressure stainless steel tubing, tested to 50,000p.s.i., was used to interconnect all pressure components. The tube terminations were cone in cone seals held together by standard Aminco

Fig. 20. Sketch of the intensifier built to develop the gas pressures needed for the experiments. The upper part of the sketch shows the cap nut bearing upon an annealed copper seal.

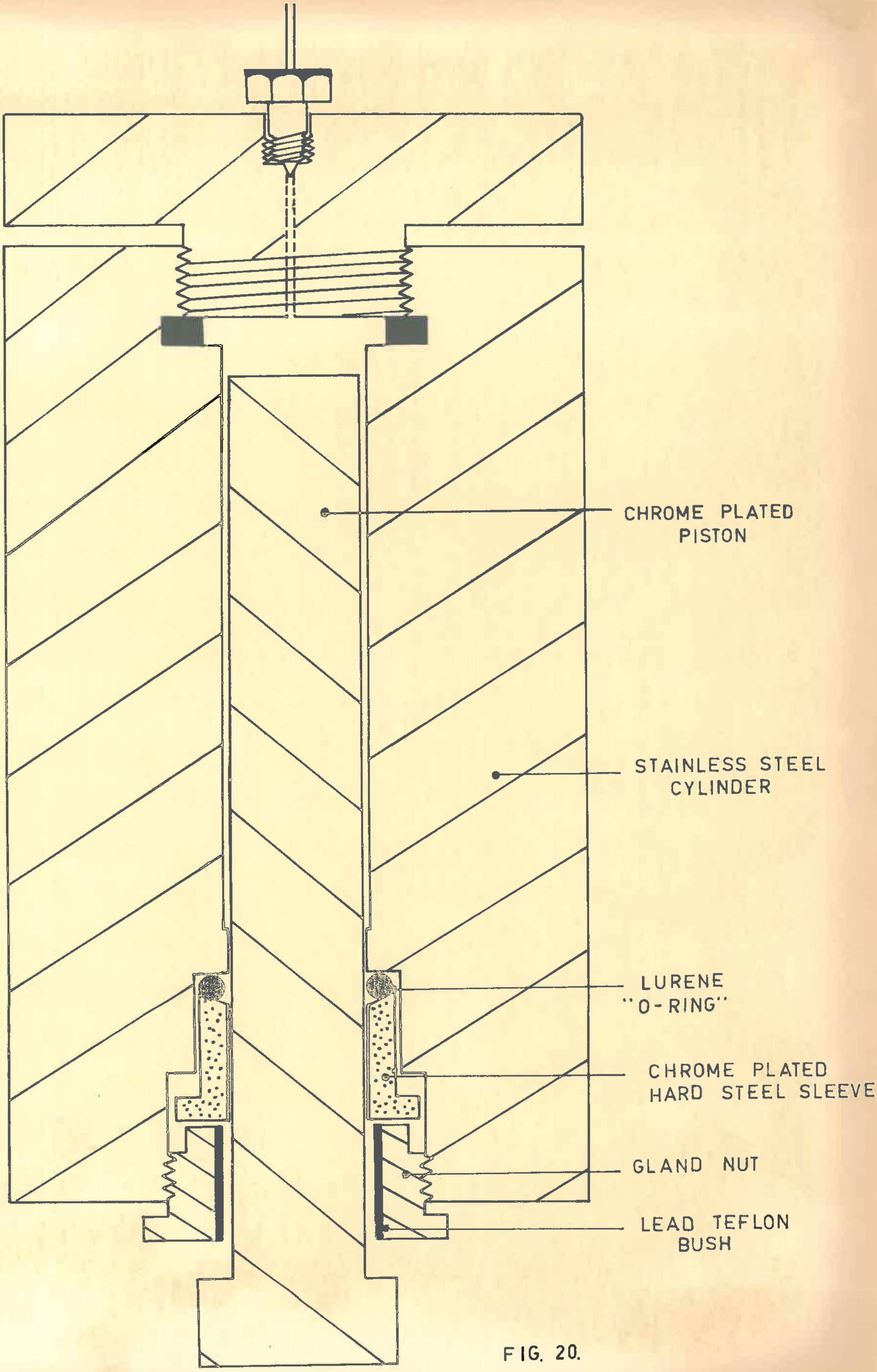

CHROME PLATED PISTON
STAINLESS STEEL CYLINDER
LURENE "O-RING"
CHROME PLATED HARD STEEL SLEEVE
GLAND NUT
LEAD TEFLON BUSH

FIG. 20.

fittings.

(b) Furnaces

Furnace construction was such that temperature gradients along the length of the platinum reaction capsule could be overcome. Gradients tend to occur naturally for two reasons:- heat losses are greater at furnace ends, secondly, and perhaps more importantly, the "cold seal portion" of the bomb is outside the furnace and therefore functions as a heat sink. By mounting each furnace on a carriage, able to move horizontally along brass rails, and by providing each furnace with two separate independently-powered windings, gradients were overcome to within 2°C.

The two furnaces each had a main winding of KANTHAL A1 and a second winding of Pt20 Rd. In one furnace the KANTHAL winding covered $\frac{3}{4}$ of the Al_2O_3 tube, the remaining $\frac{1}{4}$ was covered with the closely spaced platinum element. In the second furnace, which was more readily calibrated, the KANTHAL element covered the entire length of the Al_2O_3 tube, while the platinum winding was upon a separate ceramic sleeve moulded to fit into the furnace tube and closely round the pressure vessel. Fig 21 will make this relationship clear. Power for each winding was provided by a Variac but for

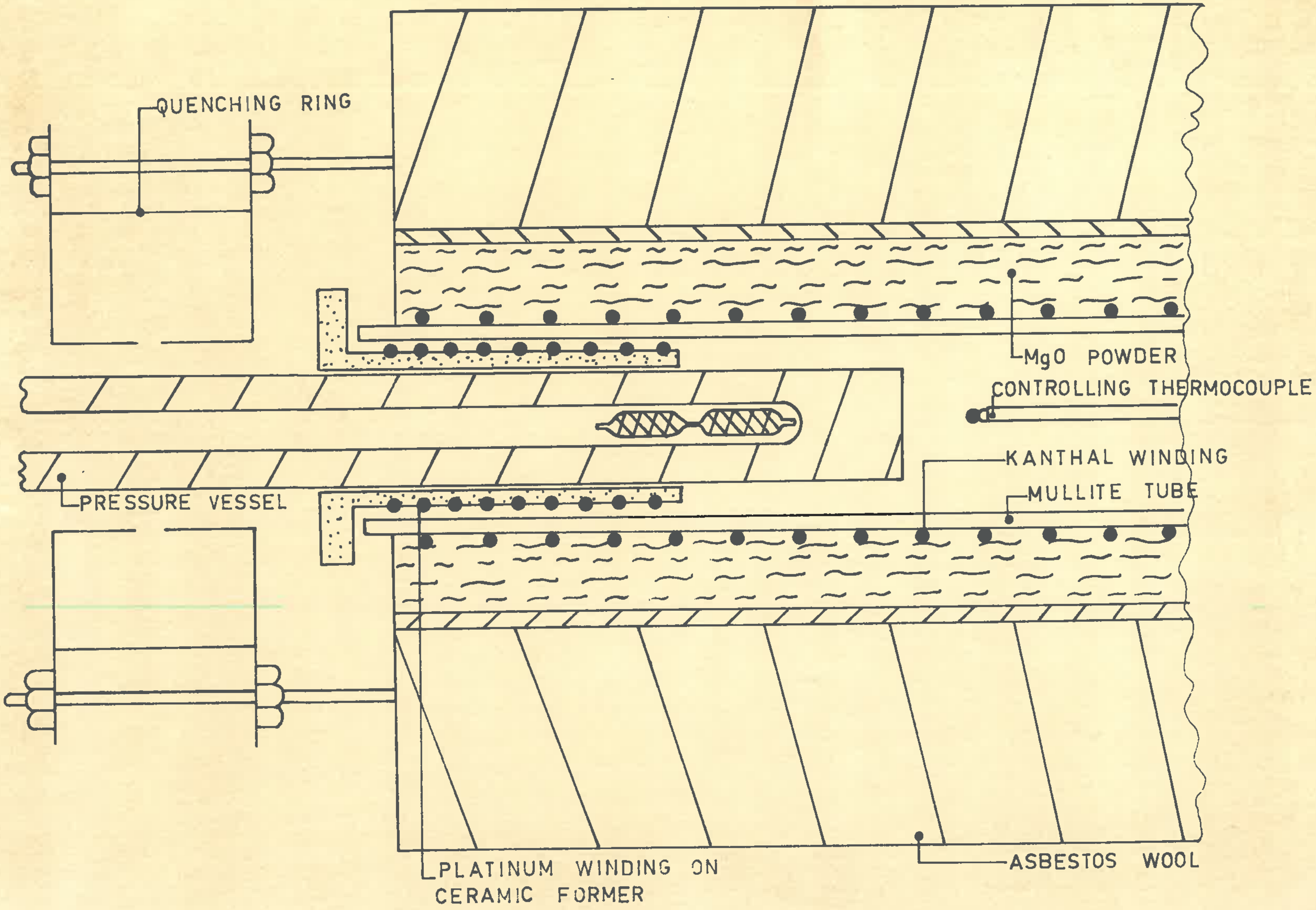


FIG. 21. CROSS SECTION OF FURNACE END. NOTE THE ATTACHED QUENCHING RING.

the KANTHAL element this was switched on and off by a relay activated from a "Capacitrol" controlled by a thermocouple in the end of the furnace.

(4) Furnace Calibration

This was achieved by installing a Pt/Pt-10Rh thermocouple in the cold seal pressure vessel mounted in exactly that position, relative to the furnace, taken up during an experiment. In practice it was necessary to remove the large union nut and other fittings attached to the bomb in order that the silica-sheathed thermocouple could be passed first to the end of the vessel and then to a position where the hot junction was about 1½" from the end. Temperature readings taken at these two positions, with a precision potentiometer, indicated the magnitude of the thermal gradient in the region occupied by the reaction capsule. Systematic adjustment of power to separate elements enabled the thermal gradient to be reduced to about 2°C.

(5) Quenching

At the end of a run, compressed air, at about 100p.s.i., was allowed to flow from a brass ring surrounding the bomb. This quenching device, seen in Fig. 22 was fastened to the furnace end and brought automatically into operating position when the furnace

Fig. 22. Close-up of furnace end showing:- quenching ring, shutter control arm and horizontally mounted pressure vessel.

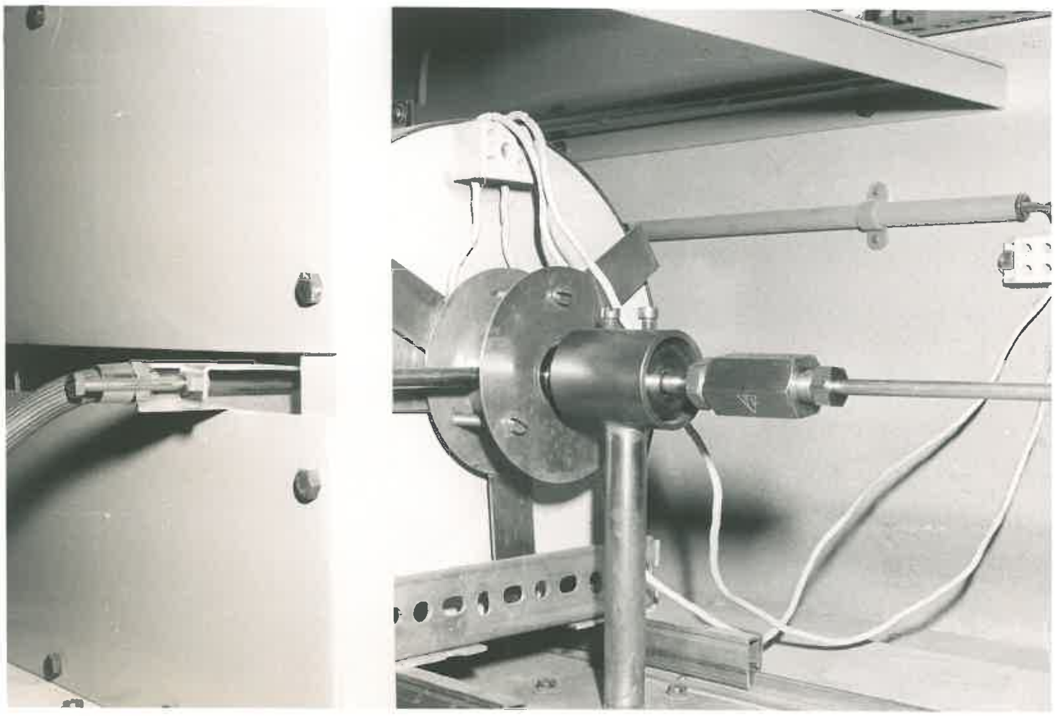


FIG. 22.

was moved away from the bomb. During quenching the end of the furnace tube was closed with a shutter. For high temperature runs approximately 3 minutes was required to reduce the bomb temperature to about 50°C.

III Determinative Methods

At the end of each hydrothermal run after the coexisting product felspars had been washed, their K, Ca, and Sr contents were measured by X-ray spectroscopy, using techniques similar to those described in chapter two. The K, Ca and Sr weight percentages were converted to weight percent felspar molecules, summed, and subtracted from one hundred percent to give weight percent albite. In addition to the bulk compositions measured on the spectrograph, X-ray powder photographs were taken of the alkali felspars, using $KBrO_3$ as an internal standard, to obtain their $\bar{2}01$ spacings.

It is important to note that not only did these films fail to suggest the presence of residual amorphous material, but also during an electron microscope examination of several low temperature products no uncrystallized material was discovered.

One of the most important problems associated with the hydrothermal experiments was concerned with the removal of excess Sr from the surfaces of grains. This Sr would presumably be attracted to crystal surfaces by unsatisfied valency bonds, such that outer layers of the crystals would have a higher ratio of Sr to other ions than would be appropriate for the crystal as a whole. In fact, high concentrations of Sr on crystal surfaces may well have been able to obscure variations in the strontium concentration of crystal lattices. The following experiment was carried out in order to test a method for the removal of surface strontium:-

After being ground to -220+300 mesh a natural potassium felspar was divided into two 250mgm portions: one was analysed for Sr on an atomic absorption spectrograph by the method of Billings and Adams (1964), the second was steeped in a one molar solution of $SrCl_2$ for 24 hours. This second portion was then transferred to a filter where it was washed with 2ml portions of 5% hydrochloric acid until the atomic absorption spectrograph was unable to detect any strontium in the wash liquid. After the acid-wash the felspar grains were rinsed several times with distilled water and reanalysed for strontium. This determination failed to reveal any difference in the strontium concentration of the treated and untreated felspars: this method was therefore adopted in preparing the hydrothermal products for analysis.

At the completion of each run the platinum capsules were cleaned on the outside before the two end compartments were clipped off with shears and carefully opened with a stainless steel probe. Each product was washed in the manner described and finally ground in an agate mortar until the particles were sized between 10 to 50 microns, at which stage they were ready for X-ray spectrographic analysis. Boric acid backed 70mgm samples were prepared in a die similar to that described by Baird (1961) (except that the central aluminium sleeve had a 0.80cm hole in it instead of 2.80cm).

The edge of the sample disc exposed to the X-ray beam was masked by a Philips aluminium-tantalum mask drilled out to 0.65cm diameter. Minor differences between the masking of the standard and unknowns were allowed for by counting on a sample disc fitted first into one holder, then the other.

(1) <u>Strontium</u>

Strontium in the synthetic felspars was determined by similar methods to those used for natural minerals, with the exception that mass absorption coefficients (μ_m values) could not be directly measured on the small amounts of material available. This difficulty was overcome by measuring μ_m values at the Sr Kα_1 wavelength, for Ab_{100}(μ_m = 6.52), Or_{100}(μ_m = 9.74), An_{30} Ab_{70}(μ_m = 7.70), and An_{75} Ab_{25}(μ_m = 9.32) "gels" which were available in large amounts. These values were plotted on two graphs i.e. μ_m Sr Kα_1 vs. Ab content of the alkali felspar and μ_m Sr Kα_1 vs. Ab content of the plagioclase. From the appropriate graphs a μ_m value for any unknown, whose composition fell between the measured end members, could be obtained. A synthetic alkali felspar containing 1200ppm was used as a substandard after it had been compared with a natural alkali felspar analysed by isotope dilution. In Table 7 are results, obtained over a period of several months, on a single felspar (H_{27} Ca Na).* From these results a standard deviation of $\approx$22 has been calculated.

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*Footnote:- H_{27} Ca Na follows the symbolism used to designate the synthetic felspars:- H indicates Hydrothermal synthesis, subscript 27 indicates experiment number 27, Ca Na indicates a plagioclase.

Sr Determinations	Differences from mean	Differences squared	
1641 ppm	38	1444	
1673 "	6	36	
1679 "	0	0	$\frac{\Sigma}{n-1}$
1698 "	19	361	
1680 "	1	1	= 465
1701 "	22	484	
mean 1679 "		Σ=2326	

Table 7. Replicate determinations for Sr on H_{27} Ca Na from which a standard deviation of 22 has been calculated.

Analyses within two standard deviations from the mean could possibly have associated with them a ±2.5% absolute error. Therefore this error has been used to calculate the limits of uncertainty associated with the strontium distribution coefficients. These limits are marked as error-bars on Fig. 28, which is a plot of the distribution coefficients (Kd_{Srf}) for strontium felspar vs. temperature.

(2) Calcium

For the plagioclases, calcium was determined by comparing the unknowns with the original synthetic "gels" for which the calcium concentrations were known. For alkali felspars, the National Bureau of Standards sample 99 (with 0.36% CaO) was a suitable standard.

(3) Potassium

A natural, well-analysed, perthite (A.U. 17263) with 11.50% K_2O was the standard used for all alkali felspar analyses. Potassium values for the plagioclases were obtained by comparison with a sodium-rich plagioclase (A.U. 16949), containing 1.19% K_2O.

The standards mentioned, were, at the inception of the experimental work, mounted in boric acid and used throughout.

The reproducibility of the calcium and potassium determinations is believed to be ±3% and this figure has been used to calculate the error-bars on the upper series of curves shown in Fig. 26 which plots distribution coefficients for albite (Kd_{Ab}) against temperature.

(4) Measurement of $\bar{2}01$ spacings of the alkali felspars and relation to composition

$\bar{2}01$ spacings for alkali felspars were measured on an 11.46 cm diameter Debye-Scherrer powder camera, using Cu $K\alpha$ radiation. Comparison of the positions of the $\bar{2}01$ reflections for the felspars with the 101 reflection of potassium bromate (101 reflection taken at 20.205°2θ for Cu Kα) yielded the 2θ separation between the $\bar{2}01$ of the felspar and the 101 of bromate. The reliability of this method is indicated by comparing the result of $d_{\bar{2}01} = 4.239$, obtained for a synthetic felspar, with values of 4.2382, 4.2372, and 4.2387 measured using a diffractometer. These separations could be used to read Mol% Or, in the alkali felspar, from a facsimile of a graph supplied by Dr. P. Orville. The reproducibility associated with compositions determined by the powder method was ±0.5% orthoclase and this value has been used to calculate the error-bars shown on the lower series of curves shown in Fig. 26.

Note: The d spacings for Ab_{100} and Or_{100} were computed by Dr. Orville from accurate cell dimension data. The values quoted for the materials prepared for the present work are based upon Dr. Orville's new value of 20.230°2θ (Cu Kα) for the 101 reflection of $K\,Br\,O_3$. By calibration against Si, Dr. Jones of the Geology Department of the University of Adelaide determined the drive rate for Brown chart recorder, used here in Adelaide, as 4.01 cm/°. This value was used in obtaining the $d_{\bar{2}01}$ values quoted.

CHAPTER IV

EQUILIBRIUM IN THE SYSTEM STUDIED

Introduction

Sr^{++}, Ca^{++}, K^{+} and Na^{+} partitioning between plagioclase and potassium felspar lattices should result in definite ratios of these ions in the lattices, if equilibrium prevails. Therefore it was important to know how long a given experiment would need to run before these ratios were reached, and if they necessarily represent a true state of dynamic equilibrium. The attainment of such a state of dynamic balance at a particular temperature would be indicated if it could be achieved both with rising, and with falling temperature conditions. This chapter will describe experiments and discuss results concerned with these problems.

I The Effect of Time

Table 9 presents results for experiments 3,4,5,9,11,15,16 and 18 which were carried out to study the variation of compositions with time.
(Complete data on all experiments is tabulated in the master-table, Table 8, which owing to size has been placed in Appendix II). For the experiments tabulated in Table 9 the starting plagioclase "gel" had a composition of $An_{30}Ab_{70}$: a pressure of 17,000psi was used throughout.

Group A experiments suggest compositions

STARTING MATERIALS		CONDITIONS		PLAGIOCLASE COMPOSITION				K-FELSPAR COMPOSITION				Expt No.	Group
Vapour	K felspar	Temperature	Time	Or	Ab	An	Srf	Srf	An	Ab	Or		
5% Sr as $SrCl_2$	$Or_{80}Ab_{20}$	520°C	3 days	7.93	66.93	22.14	2.98	6.45	1.19	21.52	70.82	5	
in H_2O.	mixed	520°C	7 days	5.18	65.82	24.18	4.80	5.17	1.71	26.45	66.65	3	A
	"gels"	520°C	10 days	5.18	66.00	24.48	4.31	5.03	4.16	27.01	66.49	4	
0.5% Sr as $SrCl_2$	$Or_{80}Ab_{20}$	850°C	3 days	6.89	64.59	26.86	0.64	0.38	1.47	28.74	69.38	9	
in H_2O	mixed	880°C	7 days	9.34	63.58	26.46	0.61	0.40	1.49	27.83	70.29	11	B
	"gels"												
0.5% Sr as $SrCl_2$	$Or_{80}Ab_{20}$	770°C	7 days	9.21	63.52	26.85	0.42	0.48	2.27	25.70	71.45	15	
in H_2O	chemically												
	produced	760°C	10 days	10.57	64.80	24.28	0.35	0.62	1.65	30.12	67.61	16	C
	"gel"	760°C	20 days	8.72	66.26	24.67	0.35	0.60	1.34	28.38	69.68	18	

Table 9. Results of experiments carried out to test the effect of time on the resulting felspar compositions. For all experiments the starting plagioclase "gel" was $An_{30}Ab_{70}$.

were still changing after 3 days, but after 7 days compositions seem to have reached relatively constant values. As a high strontium concentration was used in these runs they were repeated at approximately 860°C and 760°C with a strontium concentration of 0.5% in the vapour phase. Somewhat surprisingly, at least 7 days seems to have been needed to produce a close approach to equilibrium at the higher temperatures (groups B and C). In group C experiments, for which the alkali felspar "gel" was chemically produced with a composition of $Or_{80}Ab_{20}$, 10 days were needed to attain equilibrium at 760°C.

In connection with these equilibrium discussions it is important to note for group A experiments, where the temperature was 520°C and the alkali felspar was grown from a "gel" made by mechanically mixing in a 1:5 ratio Ab_{100} and Or_{100}, the time for "equilibration" was less than in those higher temperature experiments which used a chemically produced alkali felspar "gel" $Or_{80}Ab_{20}$. It is likely that a "gel" with an intimate admixture of components will crystallize more rapidly than a "gel" made up from end members and mechanically mixed. If so, it suggests that attainment of equilibrium between solid crystalline phases is slower than the rate of crystal growth. Rapid initial crystallization may therefore be a barrier to rapid achievement of equilibrium, because entrained ions will take a considerable time to get out of unfavourable sites. If the reactions which take place between the crystalline phases are very much slower in one direction than the other, a state of metastable equilibrium may be all that is achieved.

II Reversibility

A useful test for equilibrium is the reversibility of the reaction concerned. The results of holding charges at a lower temperature after crystallization at a higher one are collected together in Table 10.

As can be seen, little change takes place after crystallization at the higher temperature; once phases appropriate to a high temperature have been formed redistribution appropriate to a lower temperature appears to be very slow. Therefore instead of compositions appropriate to 520°C, compositions very similar to either a 660° run (cf expts. 31 and 34 with expt. 17) or a 760°C run (cf expt. 39 with expt. 16) are formed.

The results for experiments 38 and 40 (see the master table, Table 8) further demonstrate the difficulty of reversing an exchange reaction. Two "gels" with compositions $Or_{66.2}$ $Ab_{31.2}$ $An_{2.0}$ $Sr_{0.6}$ and $Or_{9.5}$ $Ab_{70.7}$ $An_{19.4}$ $Sr_{0.4}$ (similar to those of the crystalline products formed at 760°C) were prepared and crystallized together at 515°C in the presence of a vapour containing:- 1. 2500ppm Sr in water, (expt.38).

2. 1M alkali choride, K/Na+K = 30% (expt. 40).

For both experiments, instead of obtaining compositions appropriate to a 515° run (see expt. 12) compositions very similar to the original "gels" resulted. Apparently the ratios of Na and K (between tha alkali and plagioclase felspar phases) appropriate to the higher temperature are at least metastable at the lower temperature.

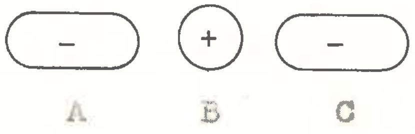
This inability to achieve reversibility does not necessarily mean equilibrium has not been reached, but it certainly suggests that any adjustment of felspar compositions with falling temperature is slow. Perhaps this is not an unlikely result if it is considered that once an ion is sited in a crystal lattice it will be held by powerful electrostatic bonds. At a given temperature these bonds will be opposed by thermal vibrations. At a reduced temperature, where thermal vibrations are damped, disruption of the bonding forces

CONDITIONS	PLAG. COMPOSITION				K-FELSPAR COMPOSITION								DISTRIBUTION COEFFICIENTS						
Temp. Time	Or	Ab	An	Srf	Bulk				(K_2O) by $\bar{2}01$ method				From Bulk comp.			From $\bar{2}01$ K_2O			Expt. Number
					Srf	An	Ab	Or	Or	Ab	An	Srf	Kd_{Srf}	Kd_{Ab}	Kd_{An}	Kd_{Srf}	Kd_{Ab}	Kd_{An}	
520°C 10 days	4.37	66.55	28.58	0.51	0.44	1.09	18.12	80.35	93.82	4.65	1.09	.44	.866	.272	.038	.087	.070	.038	12
650°C 10 days	3.64	67.61	28.36	0.39	0.61	.77	23.51	75.10	82.82	15.79	.777	.611	1.572	.347	.027	1.579	.237	.027	17
760°C 10 days	10.57	64.80	24.28	0.35	0.62	1.65	30.12	67.61	74.94	22.83	1.666	.626	1.781	.465	.068	1.799	.352	.069	16
660°C for 7 days then 520°C for 10 days	3.07	69.34	27.18	0.41	0.606	1.08	22.71	75.61	84.19	14.12	1.08	0.61	1.495	.327	.04	1.499	.204	.039	31
660°C for 7 days then 520°C for 20 days	1.87	69.51	28.21	0.41	0.620	.88	22.77	75.72	83.35	15.14	0.89	0.63	1.53	.328	.03	1.54	.218	.031	34
760°C for 7 days then 520°C for 20 days	7.73	64.62	27.22	0.42	0.65	2.34	27.44	69.57					1.51	.425	.09				39

Table 10 Results of experiments relating to reversibility of exchange equilibria. 0.5% in vapour phase; K-felspar "gel" starting composition $Or_{80}Ab_{20}$; plagioclase "gel" $An_{30}Ab_{70}$ and a pressure of 17,000 p.s.i. were common to all experiments.

will be less, i.e. the system moves to a lower energy state representing greater stability. It will, therefore, be more difficult for an ion to leave a lattice site. Since the oscillators will not have one definite frequency, but rather a distribution, a small percentage of ions may be able to escape from lattice sites, at a given temperature. However as the temperature falls more and more oscillators will occupy the lower energy states so that the percentage of ions able to escape from lattice sites will fall. In practice the situation will be complicated by geometrical distortions of the lattice; these may oppose a given pattern of electrical interaction.

In contrast to this sluggishness the work of Bowen and Tuttle (1958) demonstrated that Na-K felspars unmix, with falling temperature, quite readily. This can also be considered on the basis of energetics. Consider the potential energy of a cation (Na^+ or K^+) situated intermediate between two regions of -ve charge within a crystal (i.e. vacant cation sites) thus



At considerable separations of A and B the force of interaction will be small but as they approach the electrostatic attraction will increase, while at still closer distances there will be a violent repulsion (as a result of both internuclear interaction and overlap of electronic clouds). Fig 23(a) represents the potential energy vs. internuclear separation curve. A similar curve will result when B approaches C, only reversed from left to right because in this case the moving ion is to the left of the stationary region of -ve charge. The complete curve thus has a minimum at each end, with a horizontal portion between them; Fig. 23 (c). From the shape of this curve it is apparent that considerably less energy is required to move B from site A to site C than to move B completely from the region of A and C. Although the case considered is highly idealized and only two dimensional, the situation in a real crystal will not be too different. Thus exsolution (which involves moving cations about within the crystal lattice) can take place more easily than cation exchange between crystals (which involves moving ions over very high potential energy barriers at the crystal surface). It should be noted that if the curves drawn in Fig. 23 are for a

Fig. 23. Potential energy vs. internuclear separation, (r) for the system A + B + C discussed in the text. (C) is quite hypothetical as it does not suggest that an infinite three dimensional array of P.E. minima is involved; but in spite of this it does illustrate the difficulty of completely removing a cation from within the crystal.

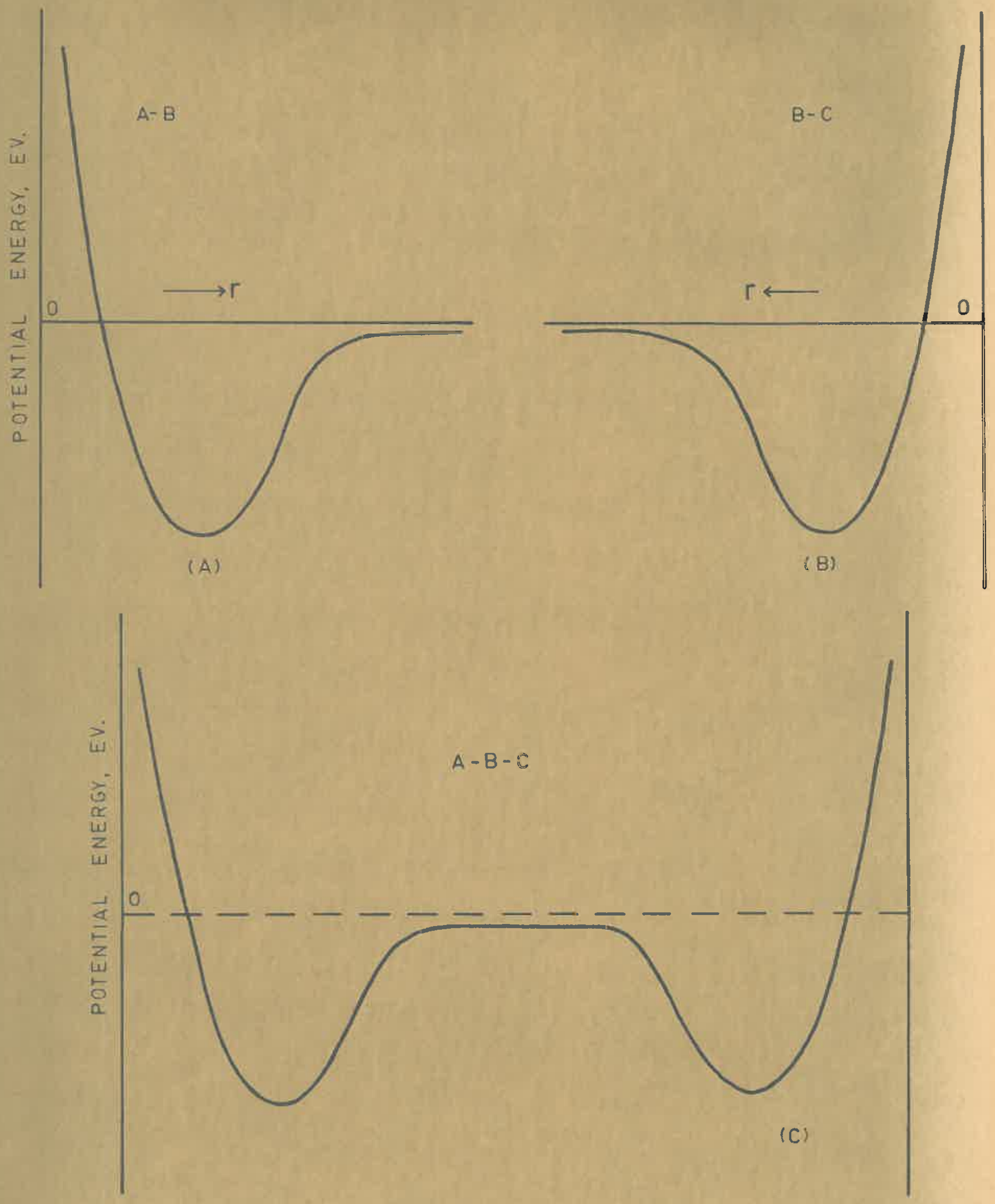


FIG. 23.

Na-O arrangement, then for a K-O arrangement the minima in the P.E. curves will not only be shallower but also will occur at larger values of r since K^+ is a larger ion than Na^+.

III Comparison of Orthoclase contents, of alkali felspars, deduced from X-ray spectrographic and $\bar{2}01$ measurements.

Orville (1963, 1966) has refined the indirect method of Bowen and Tuttle (1958) for determining alkali felspar compositions by measuring the variation in $d_{\bar{2}01}$. In the present study compositions obtained by this method commonly did not agree with the bulk compositions obtained by spectrographic analysis, as shown in Table 11. These discrepancies result from diluting albitic phases which are present in the potassium-rich phases. Evidence for this comes from the presence of high-albite lines in the powder photographs of the alkali felspars. With increasing temperatures the amount of albite in solid solution in the potassium felspar increases, hence, for a given bulk composition, the amount of diluting free albite becomes smaller. This can be seen in Table 11, where with increasing temperature, the orthoclase values obtained from $d_{\bar{2}01}$ and the X-ray spectrograph gradually approach each other. At a

Experiment	Orthoclase Content of Alkali Felspar		Temperature °C	Starting Material
	Orville's Method	X-ray Spectrograph		
6	92.8	81.1	520	$Or_{80}Ab_{20}$ mix
8	81.0	75.0	660	
7	73.5	69.0	770	
11	69.4	70.3	880	
12	92.8	80.4	520	$Or_{80}Ab_{20}$ chemically produced "gel"
17	82.0	76.1	650	
18	75.6	69.7	770	
24	89.0	74.4	515	$Or_{80}Ab_{20}$ "gel"
25	78.9	72.9	650	
26	71.3	62.8	765	
28	64.8	66.3	840	

Table 11. Showing comparison of bulk composition of alkali rich phases with actual felspar composition. An andesitic plagioclase product was present also in experiments 6-18 and an oligoclase in experiments 24-28.

definite temperature, depending on the bulk composition of the system, the albite phase will be resorbed by the potassium felspar and a further temperature increase can only produce a more albitic alkali felspar by exchanging Na with the plagioclase.

The possibility that the albitic phase, associated with potassic phase, represents contamination by plagioclase from the opposite end of the reaction capsule must not be overlooked. This was disproved for several 520° and 650° samples by measuring $d_{\bar{2}01}$ values for the albitic plagioclase and the major, more calcic plagioclase. Differences of the order of 0.009Å were observed, showing that the plagioclases are not one and the same material. With the exception of one experiment it was not possible to obtain accurate data on the compositions of the albitic alkali felspars as the small amounts present produced only weak $\bar{2}01$ lines. However experiment 12, a 520°C run, produced enough albitic material to allow estimation of its composition as Or_{10} Ab_{90}.

Another possibility is that the albitic phase represents an exsolution product formed during quenching. This has been disproved by experiment 11, which shows agreement between the bulk and the

$d_{\bar{2}01}$ composition for the alkali felspar quenched from 880°C. The tendency for albite exsolution will be greatest for a lattice containing the greatest amount of sodium, viz, the lattice formed at the highest temperature. In other words the driving energy for exsolution should be greatest for the lattice cooled from the highest temperature. Since experiment 11 presents no evidence for exsolution it is unlikely that quenching from lower temperatures was more effective.

The sketch diagrams in Fig. 24 illustrate, in a general way, the relationship between the bulk composition of the calcic plagioclase, the bulk composition of the alkali felspar phase and the compositions of the potassic and sodic components of that phase. With increasing temperature, the potassium felspar becomes more sodic, not only by resorbing the albite phase, but also by taking up sodium, released from the plagioclase. This is accompanied by loss of potassium to the plagioclase. The presence of the albitic phase in the K-Na compartment is an expression of limited solid solubility of Na-K felspars. Laves (1951) discovered limited solid solubility exists between albite and anorthite. This has the implication that for certain plagioclase

Fig. 24. The lines in the triangular plots have been drawn only to emphasize compositional changes of phases formed in the experiments.

● represents the bulk composition of the alkali felspar phases

△ represents the hypothetical composition of the albite formed in the K-Na compartment.

L represents the limiting composition the albite might have before it is finally resorbed. This composition depends upon the bulk composition of the system.

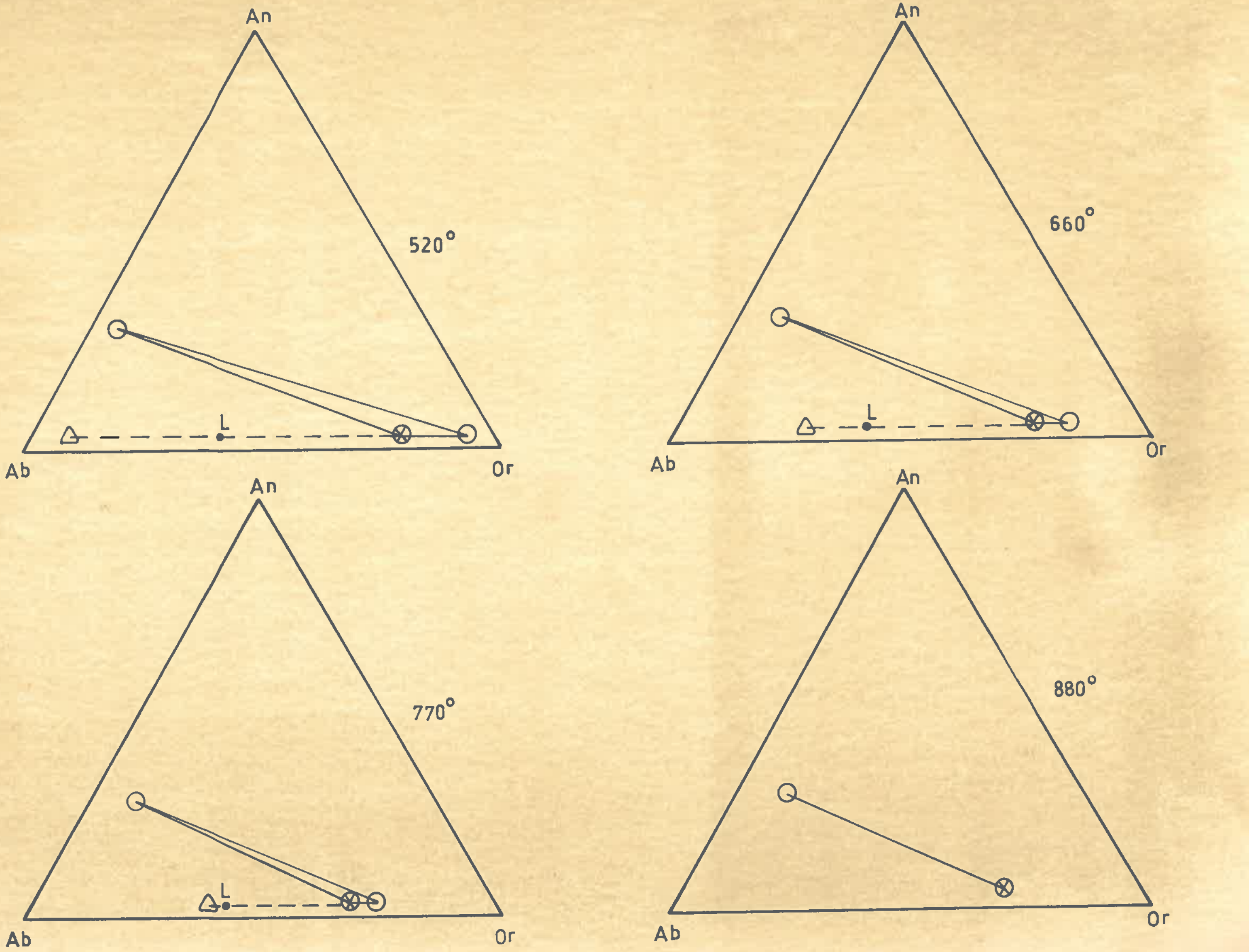


FIG. 24. PLOTS OF COMPOSITIONS OF COEXISTING SOLID PHASES AT SEVERAL TEMPERATURES

compositions (the range An_5 to An_{17}, given by Laves (1954), will be modified by temperature) an albitic phase ($An_5 \rightarrow An_{3\pm2}$) and a more calcic phase ($An_{17} \rightarrow An_{23\pm2}$) should grow in the Na-Ca compartment. Because lattice parameters of high temperature (disordered) albite and oligoclase are so nearly alike (Smith (1956)), X-ray detection of two phases in the plagioclase compartment is not expected to be successful (see Appendix III). Attempts to crystallize material coarse enough for single crystal work may however be useful, but, within the framework of the present study, time and apparatus for this was not available. However, in spite of a shortage of experimental data, subsolvus felspar relations can be postulated.

By a series of hypothetical isothermal contours, drawn on the surface of the solvus dome, an attempt has been made, in Fig. 25, to represent these relations.

At low temperatures the coexisting solid phases might have compositions represented by the points 1, 1^2, 1^3, 1^4. With increasing temperature these compositions will change through 2, 2^2, 2^3, 2^4, etc., to 5, 5^2, 5^3, 5^4 at which stage a further small temperature increase will allow full solid solution for the plagioclase felspar. At this stage an albitic phase

Fig. 25. Showing hypothetical isothermal contours on the surface of the solvus dome. For any one temperature coexisting solid phases are shown thus $1, 1^2, 1^3, 1^4$.

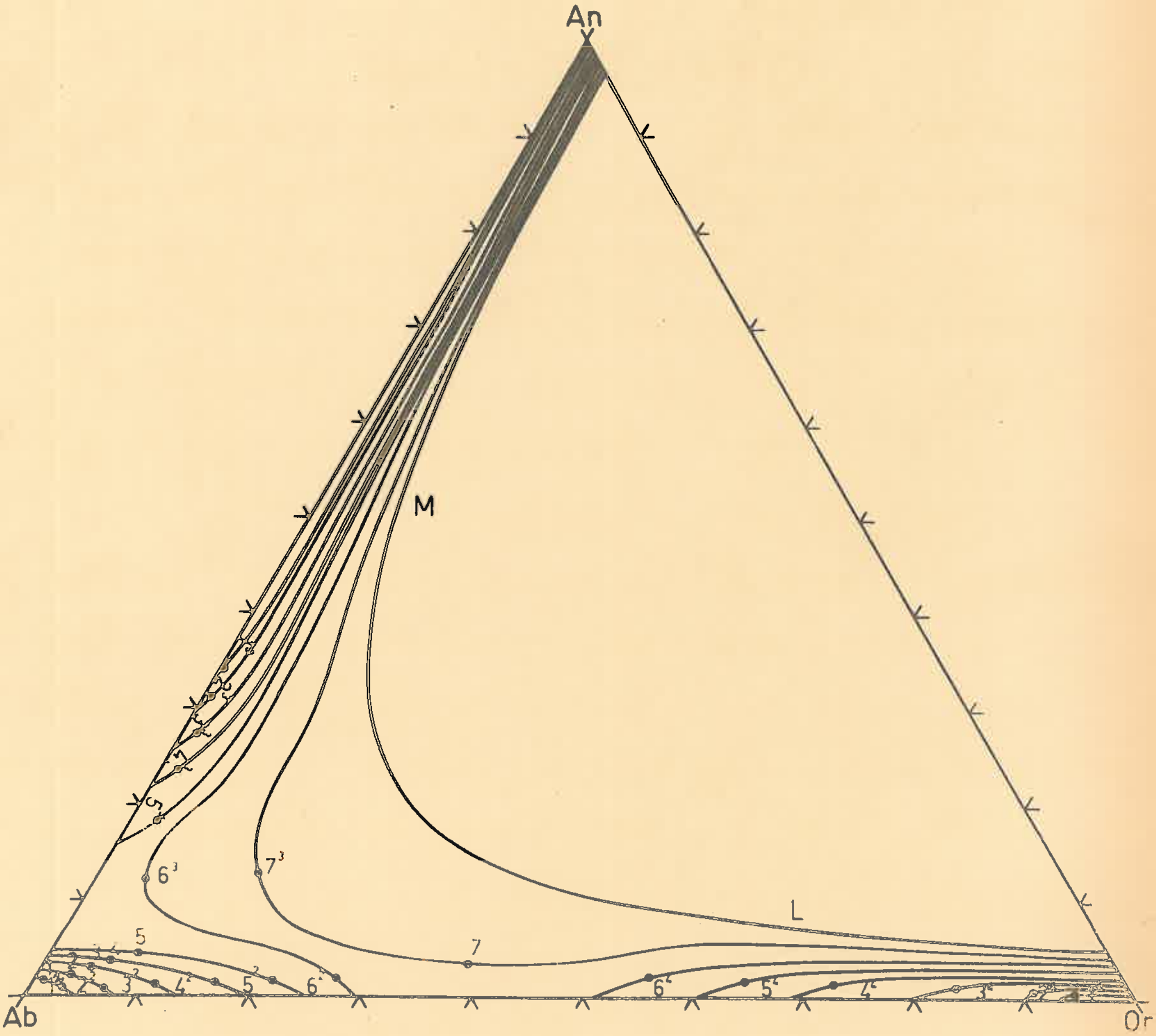


FIG. 25.

may still coexist with the potassium felspar, this situation is represented by 6^3, 6^2 and 6^4. Just above the top of the alkali felspar solvus the only solid phases will be 7 and 7^3. If the bulk composition of the system then lies to the left of the curve ML, which represents the extent of ternary solid solution, 7 and 7^3 will come slowly together to form a single phase. If the bulk composition, on the other hand, is to the right of ML, a plagioclase and a single alkali felspar must coexist.

From this discussion of Fig. 25 it can be seen that the plagioclase and the potassium felspar crystals act to some extent like closed systems in themselves, and only at relatively high temperatures might Al and Si be exchanged. In practice even this exchange will be very slow.

IV The effect of bulk composition of the whole system

Table 12 presents results from the master table, Table 8, showing how the potash contents of the K-felspar lattices and hence the albite contents from which the Kd_{Ab} values, also quoted in Table 12, are influenced by the bulk composition of the system. An inspection of this table shows that the potash content of the K-felspar is decreased in those systems

	COMPONENTS OF THE CLOSED SYSTEM			
	$Or_{80}Ab_{20}/Ab_{70}An_{30}$ + H_2O + $SrCl_2$	$Or_{80}Ab_{20}/Ab_{85}An_{15}$ + H_2O + $SrCl_2$	$Or_{80}Ab_{20}/Ab_{25}An_{75}$ + H_2O + $SrCl_2$	$Or_{98.7}Ab_{70}An_{30}$ + 2m K/K + Na = 30% + $SrCl_2$
Temperature °C	Orthoclase content of the K-felspar			
Ω520°	^{12}93.82 $_{(.070)}$	^{24}89.34 $_{(.115)}$	^{30}89.66 $_{(.320)}$	^{21}91.16 $_{(.115)}$
Ω660°	^{17}82.82 $_{(.237)}$	^{25}79.19 $_{(.242)}$	^{35}88.00 $_{(.646)}$	^{23}86.74 $_{(.186)}$
Ω770°	^{16}74.94 $_{(.352)}$	^{26}71.43 $_{(.358)}$	^{32}87.06 $_{(.369)}$	-
880° for 11 840° for 28	^{11}69.63 $_{(.448)}$	^{28}65.01 $_{(.446)}$	-	-

Table 12. Orthoclase contents of the K-felspar lattice, and distribution coefficients for albite, for several temperatures, correlated with the components of the closed system. Expt. numbers (Table 8) are given in the top left-hand corners of the compartments. Distribution coefficients for albite, from $\overline{2}01$ K_2O values, are given in brackets in the lower right-hand corners of the compartments.

rich in sodium, and that it is raised when the system is depleted in sodium, either by raising the potash content directly or by increasing the anorthite content of the plagioclase. In other words equilibrium is displaced towards high potassium in the potassium felspar when potassium in the environment is high. This important result is believed to have a direct bearing upon the unsuitability of the sodium geothermometer for application to metamorphic rocks (see Figs 1(a) and (b) and 2(b) and (c) Chapter I).

At this stage it is also interesting to note that the anorthite content of the potassium felspar (see Table 8) is very little influenced by the calcium content of the plagioclase, e.g. compare experiments 24 and 26 with 30 and 32. The amount of anorthite taken into the potassium felspar seems to be very restricted, in fact quite comparable to the amount present in natural potassium rich felspars (Deer, Howie and Zussman (1963); Smith and Ribbe (1966)).

V <u>The presence of Analcime</u>

The lowest temperature at which a partitioning experiment was carried out was 465°C, i.e. expt. 29. When the material from the Na-Ca compartment was X-rayed not only was the normal pattern for high albite obtained but also two extra lines at 5.60 and 3.42 A° were well developed. These lines almost certainly belong to analcime (with its two strongest lines at 5.61 and 3.43); although it may not be pure for in the calcium-rich environment there may well be some solid solution between analcime and Wairakite, its calcium analogue (Coombs (1955)). For the plagioclases formed at 520°C or above no analcime was detected during their X-ray examination. Mackenzie (1957) reported that the diffraction pattern for albite crystallized at 400°C and 14,000 p.s.i. contained the two strongest lines of analcime. At 300°C and 28,000 p.s.i. the only phase he could detect was analcime, however at 500°C and 14,000 p.s.i. he could detect analcime neither by X-rays nor optically. Thus at approximately 1 kilobar P_{H_2O} and between 500° and 465°C analcime begins to become a more stable phase than high albite. This tendency for analcime to form imposed a lower temperature limit on the partition experiments.

Summary

Experiments described in this chapter have shown that coexisting felspars, grown from amorphous "gels" reached fixed compositions, at a given temperature, after intervals somewhere between 7 and 10 days. In the time available it was not possible to determine whether runs of duration much greater than 20 days would alter the apparently persistent meta-stable equilibrium reached. A carefully controlled series of experiments of long duration to test the approach to stable equilibrium or alternatively the persistence of metastable equilibrium would be of immense value. Other experiments, however, have failed to show that a state of dynamic equilibrium exists between the coexisting felspar phases. Rather they have indicated that, once crystallized, felspars adjust their compositions very little with a fall in temperature.

Several experiments (38 and 40) suggest that "gels" with compositions appropriate to high temperature felspars will crystallize at a lower temperature, with little or no change in the concentrations of Na^+, Ca^{++} and K^+ which are structurally important to the product felspar. This was found to be true even though high concentrations of Na^+ and K^+ were present in the vapour phase. The situation with respect to Sr^{++} was different to that for the other cations; its concentration in the plagioclase rose, and in the potassium felspar fell, with respect to the starting materials. Sr^{++} is not significant in determining the overall structure of the phase, and, as a consequence, seems more mobile. This may be important for the success of the strontium geothermometer.

CHAPTER V

PARTITIONING OF Na AND Sr BETWEEN FELSPAR PHASES AND CRYSTAL CHEMICAL IMPLICATIONS

I <u>Distribution coefficients for albite</u>

These have been calculated on the basis of two sets of data:-

1) The <u>bulk</u> potassium contents of the potassium rich phases, as measured with the X-ray spectrograph.

2) Potassium contents of the potassium felspar <u>lattices</u>, using $\bar{2}01$ spacings.* Distribution coefficients calculated from these data are tabulated in Table 13 and plotted in Figs. 26 and 27. Only for those high temperature experiments, in which the free albitic phase was not present, do coefficients calculated from the two sets of data agree.

Inspection of Fig. 26 reveals that distribution coefficients for albite, calculated from spectrographic K_2O values, increase with temperature up to limiting values which are perhaps influenced by bulk composition of the system. Except for experiments 30, 35 and 32,

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* <u>Footnote:</u>

For these calculations it has been assumed that the albitic phase, associated with the potassium felspar, was not present. On this basis then, Sr and Ca, measured on the X-ray spectrograph, have been assigned to the potassium felspar. The Srf and An so obtained have been added to the Or, obtained by the $\bar{2}01$ method, and the resultant subtracted from 100% to give mol% albite in solid solution in the potassium felspar lattice.

Table 13 Distribution coefficients for albite tabulated for a range of temperatures and compositions

STARTING MATERIALS		CONDITIONS		DISTRIBUTION COEFFICIENTS		Expt No.
K SPAR	PLAG	TEMP	TIME	From bulk composition	Based on $\bar{2}01$ values	
$Or_{80}Ab_{20}$ "mix"	$An_{30}Ab_{70}$	520°	10 days	0.293	0.068	10
"	"	660°	7 "	0.356	0.262	8
"	"	770°	7 "	0.446	0.363	7
"	"	880°	7 "	0.437	0.448	11
$Or_{80}Ab_{20}$ "gel"	"	520°	10 "	0.272	0.070	12
"	"	650°	10 "	0.347	0.237	17
"	"	760°	10 "	0.465	0.352	16
"	$An_{15}Ab_{85}$	465°	10 "	0.280	0.109	29
"	"	515°	10 "	0.300	0.115	24
"	"	650°	10 "	0.320	0.242	25
"	"	700°	10 "	0.437	0.351	37
"	"	765°	10 "	0.470	0.358	26
"	"	840°	10 "	0.428	0.446(.446)	28
$Or_{80}Ab_{20}$ "gel"	$An_{75}Ab_{25}$	520°	10 "	0.830	0.320	30
"	"	655°	10 "	0.670	0.646	35
		765°	10 "	0.735	0.369	32

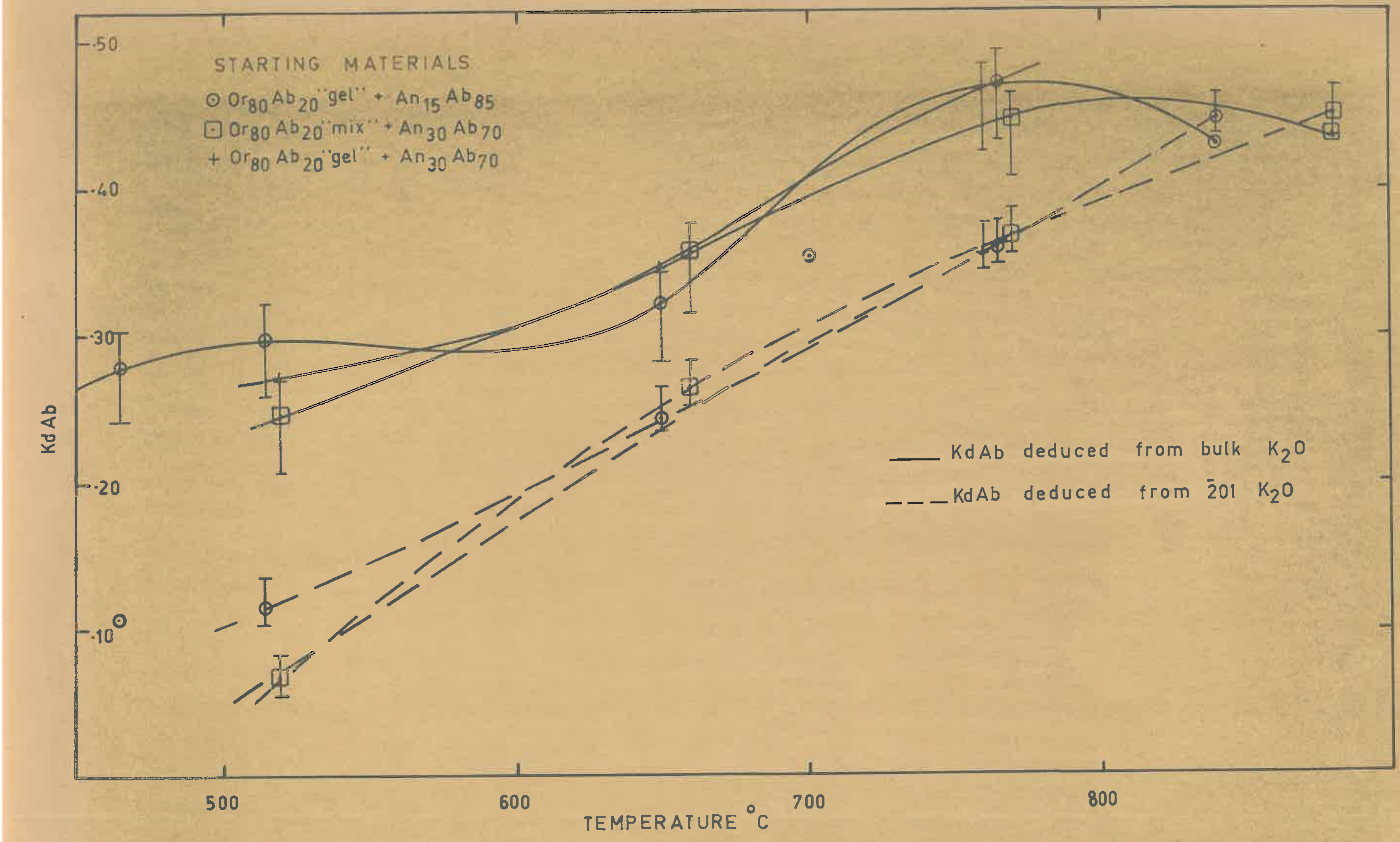

FIG. 26. DISTRIBUTION COEFFICIENTS FOR ALBITE PLOTTED AGAINST TEMPERATURE.

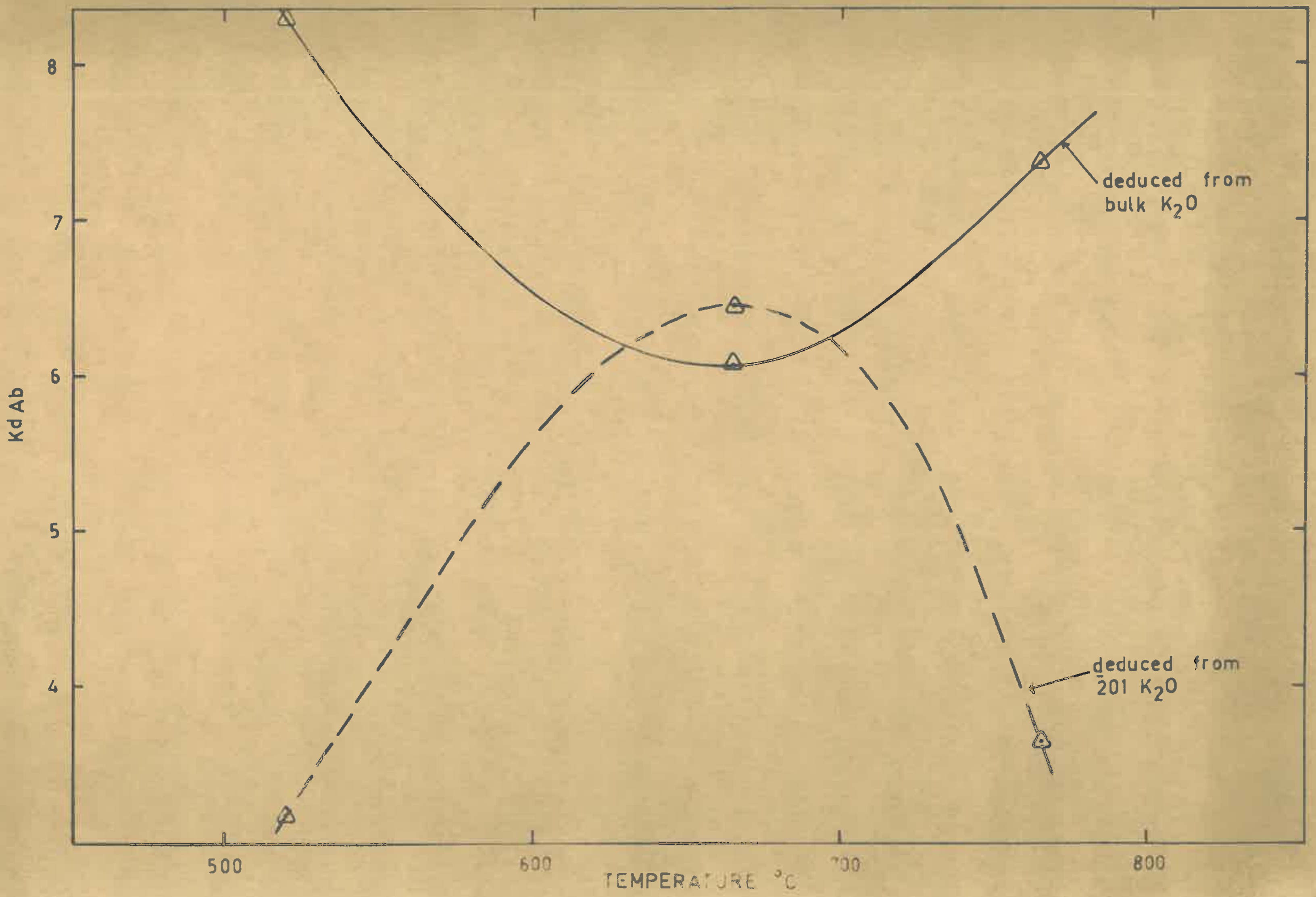

FIG. 27 ALBITE DISTRIBUTION COEFFICIENTS, AS A FUNCTION OF TEMPERATURE, IN THE CALCIUM RICH SYSTEM (EXPERIMENTS 30, 32, 35)

which had $An_{75}Ab_{25}$ as one of the starting materials, coefficients calculated from K_2O values measured by the $\bar{2}01$ method, increase continuously with temperature up to at least 880°C.

If the results for the system incorporating the calcium rich plagioclase, Fig. 27 are examined it can be seen that bulk composition has obviously influenced Kd_{Ab} values[†] calculated from both the $\bar{2}01$ and the bulk K_2O values. These results are difficult to explain in detail but they seem to express the difficulty of interchanging considerable amounts of K^+ and Na^+ in a calcium rich felspar (this is required if the necessary sodium ions are to be taken into the potassium felspar lattice). This limited substitution of K^+ for Na^+ may be determined by the plagioclase framework which is contracted about the small doubly positive calcium ions and therefore unable to admit large K^+ ions. Calcium will therefore, in natural systems, exert an important influence upon sodium distribution by controlling the plagioclase composition which initially crystallizes.

Variations in the plagioclase composition, after crystallization, will chiefly involve the limited

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[†] See also Table 12, Ch.IV.

interchange of sodium and potassium, not calcium. Not only are small amounts of calcium incorporated into the coexisting potassium felspar but also its double positive charge will tend to prevent it moving from plagioclase lattice sites and through the electrostatic field of the crystal lattice. The difficulty of moving calcium will be intensified by the required concomitant movement of sufficient aluminium to maintain charge balance. For plagioclases, then, all that is observed with increasing temperature is the limited substitution of potassium for sodium.

The behaviour of distribution coefficients plotted in Fig. 26 deserve close examination. Basically, it is the presence of the free albitic phase which is responsible for the differences between the bulk and $\bar{2}01$ based Kd_{Ab} values. At low temperatures the amount of free albite is relatively large, at the same stage the K/Na ratio for the potassium felspar is high. With increasing temperature the K/Na ratio decreases, as sodium lost by the albitic and calcic plagioclases is taken up by the potassium felspar lattice to establish a K/Na ratio appropriate to the temperature. Concurrently, potassium is released from the potassium felspar and taken up by the calcic plagioclase, and presumably also by the albitic phase. Eventually the potassium-rich and sodium-rich phases become indistinguishable, also, although we have no evidence in the present experiments for this, the calcic plagioclase presumably becomes saturated with potassium. A further temperature increase will cause potassium to be released by the plagioclase (Yoder, Stewart and Smith, 1957). Since this potassium is taken up by the potassium-rich phase, as well as by the liquid phase beginning to develop, there will be observed, in quenched experiments a fall in Kd_{Ab} values calculated from $\bar{2}01$ values.

II Distribution coefficients for strontium felspar

In Table 14 and Fig. 28 are presented a selection of data from the master table, Table 8, showing the partitioning behaviour of strontium. It can be seen from the graphs that distribution coefficients (Kd_{Srf} values) increase with temperature up to certain limiting values. For any one temperature, however, coefficients differ considerably according to whether a "mix", $Or_{80}Ab_{20}$, or a "gel", $Or_{80}Ab_{20}$, was used as one of the starting materials. The reason for this is not known, but it seems reasonable that different rates of crystallization are responsible. Rapid crystallization

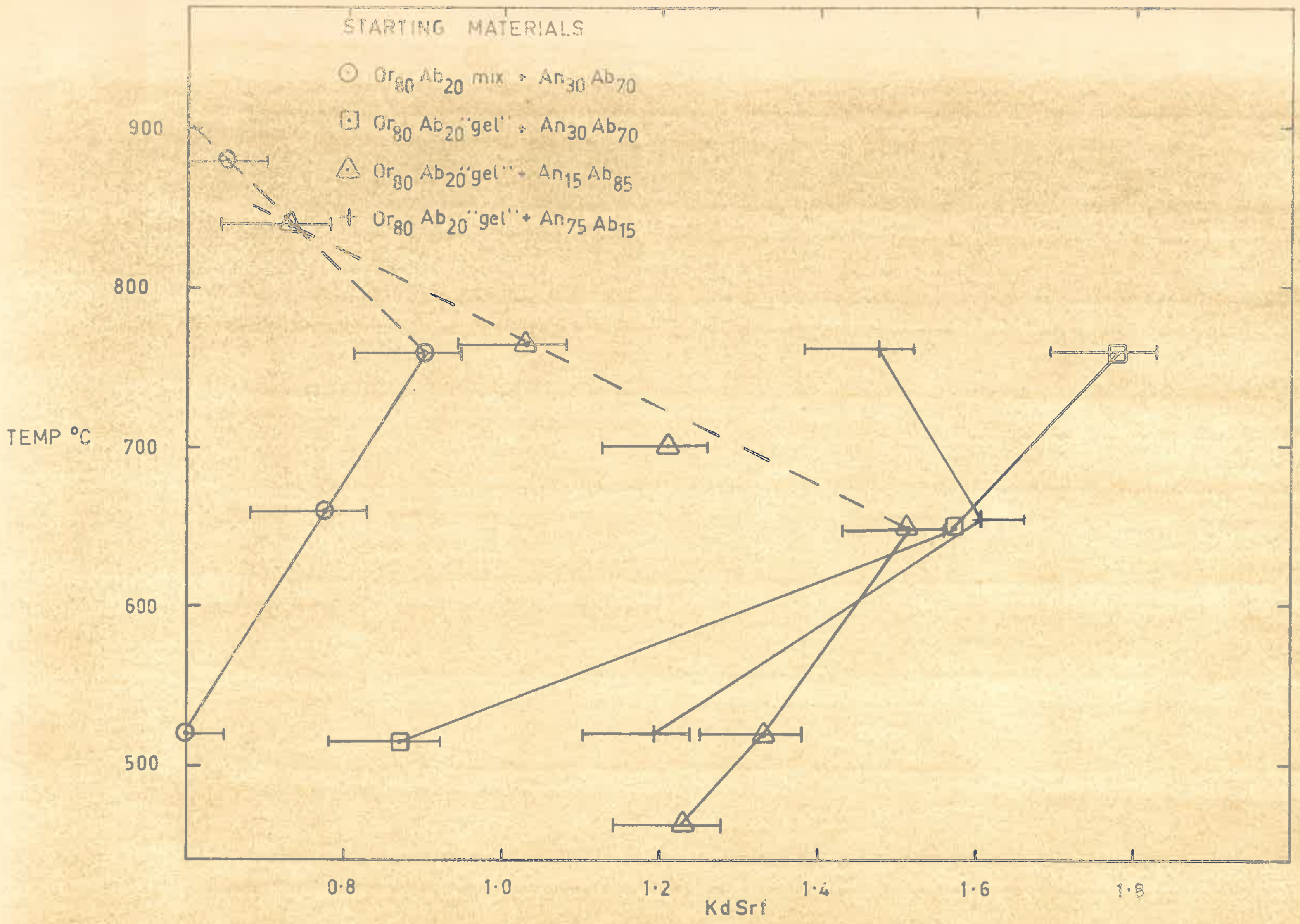

FIG. 28. EXPERIMENTAL DISTRIBUTION COEFFICIENTS FOR Srf PLOTTED AGAINST TEMPERATURE

may cause a considerable amount of strontium to become entrained in the growing crystals, rather than sited in the structure on large-cation positions. Hence varying rates of crystallization will cause varying "base concentrations" of entrained Sr to be present. Added to the base concentrations will be the concentrations of Sr actually situated in cation positions. The alkali felspar starting material was the only "phase" in the experiments which had different forms, i.e. mix or chemically produced "gel" and because of this was able to exercise an important influence on the rate of crystallization (see previous section on Equilibrium).

The presence of the albitic phase admixed with the potassium felspar modifies the measured Kd_{Srf} values, but the effect is small, as can be seen by comparing distribution coefficients calculated from $\bar{2}01$ based K_2O values and those based upon bulk composition. The diluting effect of the albite is small, since not only is it present in small amounts, but it will itself incorporate strontium (Heier, pers. comm.).

In spite of the possibilities for entrainment of strontium, and the undoubted presence of the albitic phase with the potassium rich felspars, the Kd_{Srf} values strongly suggest that strontium partitions itself between

Table 14 Distribution coefficients for strontium felspar tabulated for a range of temperatures and compositions.

STARTING MATERIALS		CONDITIONS		DISTRIBUTION COEFFICIENTS		Expt No.
K SPAR	PLAG.	TEMP.	TIME	From bulk temp.	Based on $\bar{2}01$ K_2O values	
$Or_{80}Ab_{20}$ mix	$An_{30}Ab_{70}$	520°	10 days	0.603	0.655	10
"	"	660°	7 days	0.774	0.804	8
"	"	770°	7 "	0.900	0.960	7
"	"	880°	7 "	0.645	0.644	11
$Or_{80}Ab_{20}$ gel	"	520°	10 "	0.866	0.867	12
"	"	650°	10 "	1.572	1.579	17
"	"	760°	10 "	1.781	1.799	16
$Or_{80}Ab_{20}$ "gel"	$An_{15}Ab_{85}$	465°	10 "	1.23	1.24	29
"	"	515°	10 "	1.33	1.35	24
"	"	650°	10 "	1.52	1.53	25
"	"	700°	10 "	1.21	1.21	37
"	"	765°	10 "	1.03	1.03	26
"	"	840°	10 "	0.735	0.734	28
$Or_{80}Ab_{20}$ "gel"	$An_{75}Ab_{25}$	520°	10 "	1.19	1.14	30
"	"	655°	10 "	1.62	1.62	35
"	"	765°	10 "	1.47	1.48	32

coexisting felspars in a temperature sensitive way.

The reversal of the trend of Kd_{Srf} values with temperature, at high temperatures, is not understood but the following possibilities will be examined:-

1) incipient melting.
2) geometrical effects favouring strontium substitution into the potassium-felspar lattice at low temperatures but not at high temperatures.
3) lack of charge balance.

1. Incipient melting

Examination, under oil immersion, of the high temperature products revealed no material which could be identified as glass. This does not, however, prove the absence of glass, but may just indicate the difficulty of recognizing it. The paper of Luth, Jahns, and Tuttle (1964), which gives data on the beginning of melting of felspars, has no data directly bearing on the three felspar system under discussion.

2. Geometrical effects

Before these are considered in detail some experiments which illustrate that strontium is not merely entrained, but truly occupies cation sites in the potassium felspar lattice, will be discussed. Large concentrations of calcium are not found in natural potassium-rich felspars, even in those from calcium-rich environments (see as an example sample 18L, Table 4, Ch.2). Substitution, then of a small dipositive ion for potassium, along with the necessary concomitant substitution of Al for Si, in a potassium-rich felspar, is apparently not favoured, i.e. the K-felspar lattice is not able to cope with the small (.99A°) Ca^{++} as well as the charge balance problem. However the situation is different when the larger (1.13A°) Sr^{++} ion is involved, as the following experiments are believed to demonstrate.

Two "gels", with compositions $K_{0.8}\,Sr_{0.2}\,Al_{1.2}\,Si_{2.8}\,O_8$ and $K_{0.95}\,Sr_{0.05}\,Al_{1.05}\,Si_{2.95}\,O_8$, were prepared and each separately crystallized for 4 days at 660°C and 20,000p.s.i. P_{H_2O}. Powder photographs of the products were taken, and the $\bar{2}01$ spacings of the potassium felspars were compared, on a diffractometer, with 101 spacing of $KBrO_3$. The pattern of the material crystallized from the 5% Srf "gel" was characteristic of high sanidine, but the pattern of material which crystallized from the 20% Srf "gel" was more complex. The following phases were detected:- high sanidine, mica, $Sr\,Al_2\,Si_2\,O_8$ (the triclinic polymorph? Sorrell 1962). The $\bar{2}01$ spacing of the sanidine, which crystallized from the 20% Srf "gel", was found to be 4.193 ±.001A°, whilst the value for the sanidine crystallized from the 5% Srf "gel" was 4.228 ±0.001A°. These values are to be compared with 4.235 ±0.001A° recorded for the $\bar{2}01$ spacing of a sample of Or$_{99}$ crystallized for 65 hrs. at 850°C and 17,000p.s.i. This data has been interpreted as follows.

a) appreciable solid-solution of the Srf molecule in the potassium-felspar lattice takes place at 660°C, causing a decrease in the $\bar{2}01$ spacing analogous to the decrease which occurs when Na$^+$ is substituted for K$^+$.

b) at 660°C the limit of solid solution is greater than 5 but less than 20 mol percent. This has resulted, in the case of the Srf$_{20}$ "gel", in the crystallization of a small amount of free Srf; but to use up excess Al and Si, not required for the crystallization of the Sr-containing potassium-rich felspar (>80mol%Or) a phase, viz. mica, with a lower K/Al + Si ratio grew.

c) the decrease of the $\bar{2}01$ spacing in a K-felspar containing Srf, does not seem to be a linear function of composition.

If the interpretations of the above experiments are correct, it is reasonable to believe the <u>trace</u>

amounts of Sr in natural and synthetic felspars actually occupy large - cation sites. This being so, the importance of geometrical effects on strontium partitioning can be considered.

Ferguson, Traill and Taylor (1958) showed that a marked anisotropy of the electron density distribution exists at the site of the Na atom in high and low albites. They believed the effect, which was much greater in high albite, was too large to be attributed to thermal vibration and therefore proposed that the cavity available to Na is much larger than it can fill, and hence it tends to occupy, at random, one side of half the cavities and the other side of the other half. This view was strengthened by the work, at -180°C, on the structures of high and low albites by Williams and Megaw (1964). According to Brown and Bailey (1964) the potassium atom has measurable anisotropy in all the potassium felspars studied. The ellipsoid of vibration has been determined for orthoclase by Jones and Taylor (1961), for the Pellotsalo microcline by Brown and Bailey (1964), and for the Pontiskalk microcline by Finney and Bailey (1964). The anisotropy, which in any case is very much less than in albite, has been explained as resulting from thermal vibration within an irregular coordination group.

The oscillation is restricted by four close oxygen neighbours and repulsion from an adjacent K atom along the minor axis of the ellipsoid, which is stated to be 12° off parallel with x.* The important factor which comes from this consideration of the large cation environment in felspars, including the calcium felspars, according to Megaw, Kempster and Radoslovich (1962), is that a certain amount of unfilled space exists about the Na, K or Ca environments. Consider the fit of Sr^{++} into the cation site in alkali and plagioclase felspars at different temperatures.

The following ionic radii, from Evans (1964), K^+ 1.33A°, Na^+ 0.95A°, Sr^{++} 1.13A° and Ca^{++} 0.99 are important for the following discussion. Substitution of Sr^{++} into the cation site of a plagioclase will involve local expansion, whereas considerable contraction and rearrangement will be involved in the substitution for potassium. With increasing temperature Sr and its surrounding oxygens will tend, as a result of increasing thermal motion, to occupy larger effective volumes. However since O is so much lighter than Sr the effective volumes occupied by oxygens will increase much more rapidly than those occupied by Sr. The net effect of expansions will be a movement of the oxygens' charge into the unfilled space about the Sr^{++} ion. The fit of Sr^{++} into the potassium felspar will therefore improve *until* all vacant space about the cation is filled, whereas the fit into the cation site in plagioclase will worsen. However, since the site in plagioclase is considerably elongated, and we are dealing with trace amounts of strontium, the vacant space may not be completely reduced at that temperature for which complete closure takes place for the potassium felspar. We will therefore have the situation in which Sr^{++}, above a certain unknown critical temperature, will more easily enter the plagioclase structure, but at temperatures below this it will prefer the potassium felspar lattice, since its fit will tend to improve with temperature increases up to this value. It is possible to envisage a number of geometrical effects favouring the entrance of Sr into potassium felspars at certain temperatures whilst at higher temperatures the preference is for the plagioclase lattice. The best test for the ideas concerning the cation site in felspars would certainly be structure determinations, at high and low temperatures, on both alkali and plagioclase felspars. This data is not available, but interesting indirect support is obtained from thermal expansion data.

The evidence from thermal expansion:-

If the oxygens surrounding the large cations vibrate with increasing temperature to effectively occupy the vacant ellipsoidal space about those cations, then variation in the proportion of vacant space should lead to different rates of volume expansion at high and low temperatures. This effect should be well shown by a sodium-rich potassium-felspar since substitution of K^+ by Na^+ will increase the free space (Na^+ is smaller than K^+)[*].

At low temperatures then, the increasing oxygen vibrations will be taken up in the free space about cations, as well as by the other cavities in the structure. At higher temperatures, this free space will not be avail-

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[*] Footnote:

It should be noted that although there is an almost linear decrease in a_o with sodium substitution for potassium, the major extension of the cation cavity is approximately in the (100) plane. Thus the decrease in a_o must not be taken as an indication that excess space in the cation cavity is being decreased when Na substitutes for K in a potassium felspar. For several felspars, linear expansion data, graphed in Fig. 29 suggests that orientation of the cation ellipsoid is important in determining external expansions measured in the several crystallographic directions. In each case expansion parallel to "a" is much greater than for components in the other two crystallographic directions. This result is compatable with ideas concerning collapse into free space in the (100) plane, and thereby limiting expansions along directions in this plane. Along the "a" direction free space is at a minimum hence external expansion is most marked.

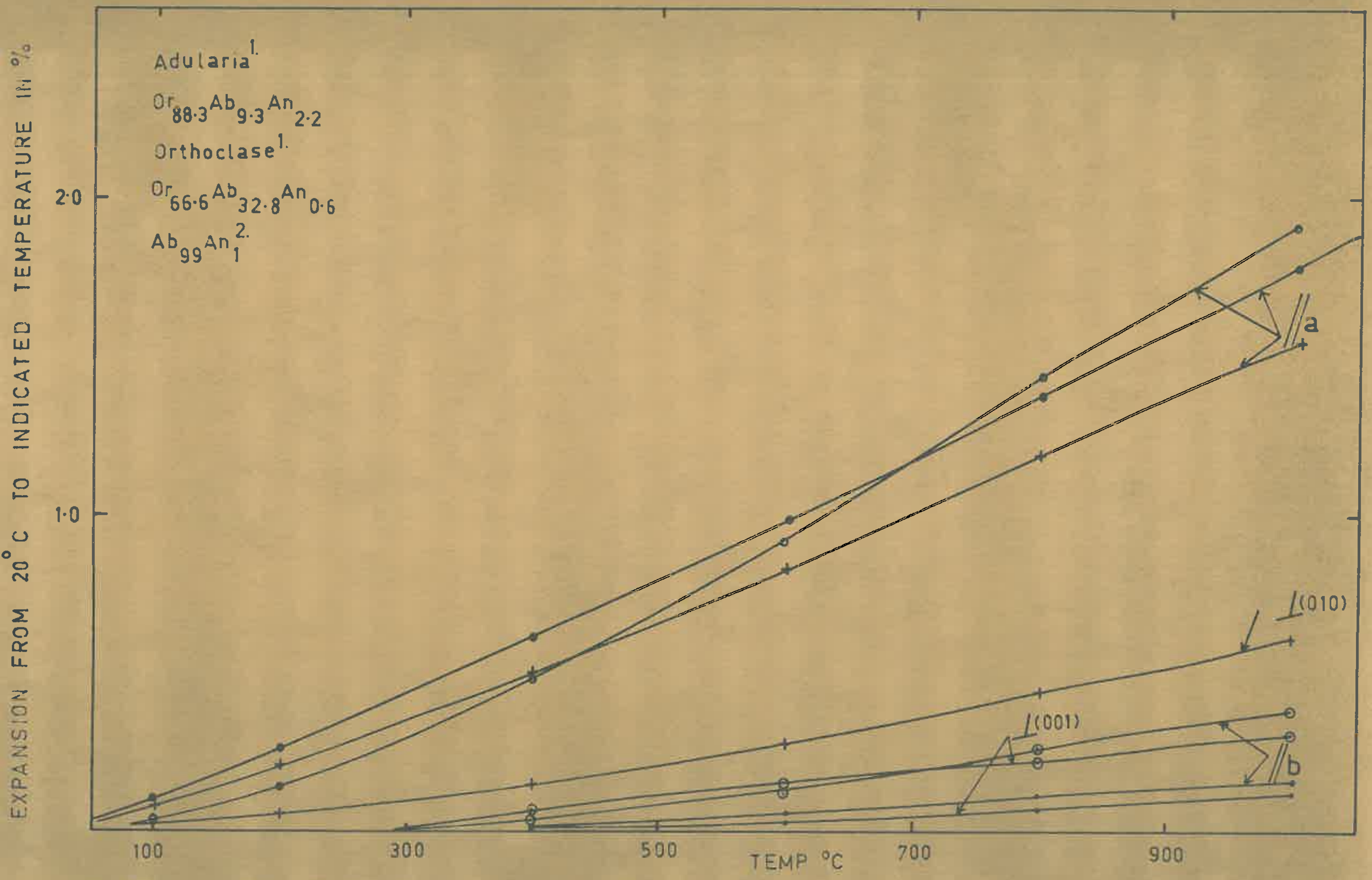

FIG 29. LINEAR EXPANSIONS, ALONG INDICATED CRYSTALLOGRAPHIC DIRECTIONS FOR THREE ALKALI FELSPARS.

1. AFTER KOZU AND SAIKI (1925).
2. AFTER KOZU AND UEDA (1933).

able to absorb the increasing "effective volumes" of oxygens, hence the external volume expansion should become more marked. This behaviour will contrast with that of a pure potassium felspar, or a pure sodium felspar.

For pure potassium felspar expansion will be more even, over a wide temperature range, because the small proportion of free space in the K^+ site will be occupied at low temperature so that further temperature increase will cause external expansion. The very elliptical Na^+ site in albites will allow considerable "internal expansion" hence the external expansion rate should not vary greatly with temperature.

These ideas can be examined in light of experimental data. Fig. 30 shows that % volume expansion (referred to the volume at 20°C) for a number of felspars of different compositions. This data obtained by Kozu and Saiki (1925), and Kozu and Ueda (1933), is tabulated, for convenience, in Table 15. From these results we observe:-

a) The increase in volume expansion for adularia ($Or_{88.3}$ $Ab_{9.3}$ $An_{2.4}$) is slightly greater at high temperatures than for equal temperature increases at low temperatures, cf. volume expansion in the range 800-1000°C

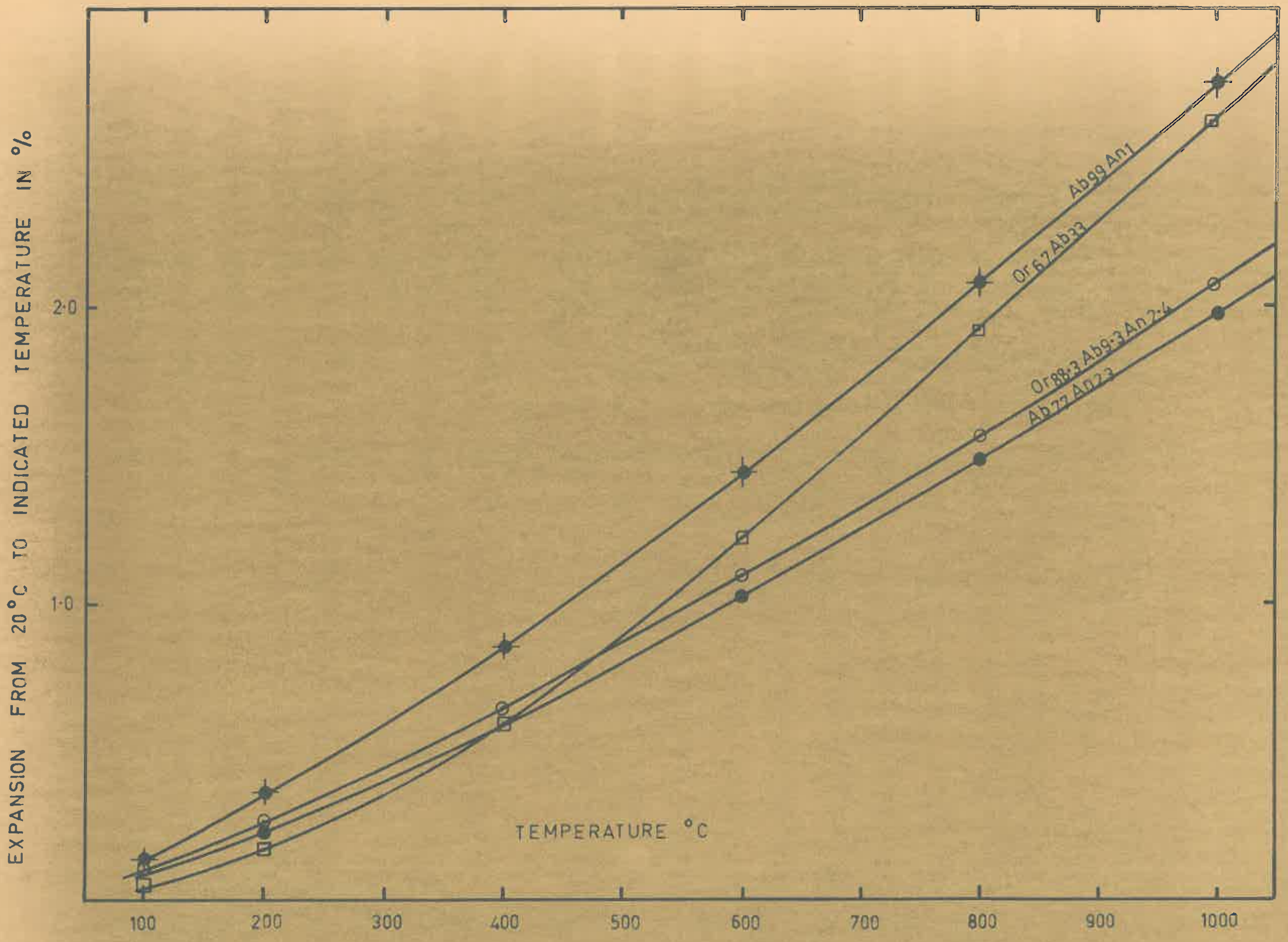

FIG. 30. VOLUME EXPANSION, FOR SEVERAL FELSPARS, PLOTTED AGAINST TEMPERATURE.

with the expansion in the 200-400°C range.

b) Albite expansion is also fairly even.

c) For Or_{67} Ab_{33} the volume increase is, as predicted, considerably greater in the 800-1000°C range than in the 200-400°C range. In addition, the actual % volume expansion (when compared with the volume at 20°C) is less at lower temperatures than for a potassium-rich phase, the expected result on increasing the internal free space.

d) The expansion of Ab_{77} An_{23} is considerably more even than for Or_{67} Ab_{33}. If this is an indication that internal space is still available at relatively high temperatures we can see how Sr substitution may continue to such temperatures.

It is realized the expansion data does not solve the problem of Sr substitution in felspars, but at least it is not incompatible with the geometrical model proposed.

In addition to its influence upon the mechanism just discussed the sodium content of the potassium felspar lattice may also be important in another way.

Natural felspars show increasing anorthite solid solution in potassium felspar with increasing Na content. Does then the increased substitution of Na for K, at high temperatures, make it easier for the potassium felspar

	Expansion from 20°C to indicated temperature, in per centum					
Composition	100°C	200°C	400°C	600°C	800°C	1000°C
$Ab_{99}An_1$ †	.14	.36	.85	1.44	2.07	2.75
$Or_{67}Ab_{33}$ †	.049	.155	.585	1.185	1.910	2.610
$Or_{88.3}Ab_{9.3}An_{2.4}$ *	.109	.269	.643	1.091	1.559	2.054
$Ab_{77}An_{23}$ †	.090	.23	.59	1.00	1.47	1.96

Table 15. Thermal volume expansions of two albitic and two potassic felspars.

† Kozu and Ueda (1933); * Kozu and Saiki (1925).

lattice to take up Sr? Expressed in another way:- does Na in a potassium felspar distort a proportion of the cation environments such that Sr will enter Na-rich domains in the crystal? Such domains if they exist may incorporate only several unit cells. If this mechanism is important it is difficult to understand how Kd_{Srf} values can fall at high temperatures where the albite content of the potassium felspar lattice is still rising.

3. Lack of charge balance

The concomitant substitution of aluminium for silicon, when strontium substitutes for either sodium or potassium, need perhaps not be operative when small amounts of Sr are involved, as charge balance may be preserved by lattice imperfections (vacancies or interstitials). This mechanism is unlikely to be sufficient for large amounts of strontium.

The experiments show that calcium leaves the plagioclase lattice and appears to enter the potassium felspar. The result will be a slight excess of Al^{+++} in the plagioclase and neutralization of some lattice imperfections in the potassium felspar. The entry of Sr^{++} will tend to neutralize the residual imperfections. If, initially, the total number of imperfections in the plagioclase was roughly equal to the total number in the potassium felspar, larger amounts of Sr will be admitted in to the plagioclase as a result of the greater number of imperfections and the excess Al^{+++}.

Even if imperfections are insufficient to maintain charge balance, the alternative, movement of Si and Al, is expected to be difficult under subsolvus conditions and will impose an upper limit on the strontium concentration in the potassium felspar. Thus, the necessity to balance charges may mean, at high temperatures, Sr^{++} can more readily enter a plagioclase than the coexisting potassic felspar.

III Conclusions

1. In closed systems albite distribution coefficients, when calculated on the basis of the sodium content of the potassium felspar phase, show a systematic increase with temperature. Alkali exchange is believed to be restricted in a system crystallizing a calcic plagioclase (An_{75}), in such systems Kd_{Ab} values do not systematically increase with temperature, (experiments 30, 35, 32). Distribution coefficients are also influenced by high Na and K concentrations in the vapour phase, (compare experiments 12 and 17 with 21 and 23).

2. Distribution coefficients for strontium, although influenced, in the experiments, by a separate

albitic phase, and perhaps by entrained strontium, are temperature sensitive. The values, measured, within the temperature range believed to characterize high grade metamorphism, even if not representative of complete equilibrium, are compatible with natural data. At an ill-defined temperature, above 660°C, distribution coefficients begin to fall with increasing temperature. A mechanism combining both geometrical and charge balance considerations is proposed to explain the partitioning behaviour of strontium. Thermal expansion data, taken from the literature are consistent with the geometrical aspect of the explanation.

CHAPTER VI

NATURAL FELSPARS CONSIDERED

IN

LIGHT OF EXPERIMENTS

I Sodium Distribution Coefficients

The experiments in the system $An-Or-Ab-H_2O-SrCl_2$ have certainly confirmed Barth's hypothesis that sodium distribution between felspars is temperature sensitive. However application of this geothermometer to natural igneous rocks needs caution; for in such rocks equilibrium between coexisting felspars is frequently not achieved. As evidence for this there is the zoning of plagioclases, and also of the coexisting potassium rich phases (W.A. Elders, pers. com.). With the electron microprobe, compositions of zones within a crystal of plagioclase could be determined, but in order to use the sodium geothermometer to follow a crystallization sequence, identification of the corresponding zones in the alkali felspar would be needed before analysis. This seems an impossible task.

In addition to the zoning which occurs as a result of melt crystallization, late stage hydrothermal, alteration, particularly in granites represents a further complication. These simple considerations suggest the sodium geothermometer will have restricted application to igneous material.

In 1956 Barth stipulated that his sodium geothermometer was only to be applied to felspars with the following composition ranges:- plagioclases 10-30% and alkali felspars 10-30% Ab. If, however, sodium distribution coefficients for what appear to be equilibrium assemblages of metamorphic felspars within these composition ranges are examined (See Figs. 1 and 2, Ch. I), an unreliable correlation with grade is found. The varying success of the geothermometer may well be determined by,

1. the bulk composition of the plagioclase which initially crystallizes, and

2. the chemical and thermal history of the alkali felspar metamorphosed.

(i) Bulk composition of the plagioclase. The composition of the plagioclase initially crystallized will, in turn, depend upon the composition of a particular portion of an unhomogeneous rock undergoing metamorphism. In this connection it is interesting to quote a passage from Mehnert (1962) in which he is discussing some work by Wenk (1958 and 1962) on high pt. plagioclases:- "Correlation of plagioclase composition with chemical variations of the parent rock is often so clear that it may be assumed that the reactions took place in an essentially closed system (with regard to the plagioclase formation). Thus, plagioclase can only serve as a geothermometer in rocks of equal bulk composition". This, combined with the experimental fact that once a plagioclase has crystallized its changes in composition with temperature are small, emphasizes the effect local variations in the original rock composition may have upon Kd_{Ab} values.

(ii) The chemical and thermal history of the alkali felspar. Consider a sodium-rich, detrital potassium felspar which originally crystallized at a temperature above the top of the alkali felspar solvus. In the context of the discussion to follow it is unimportant whether or not the felspar is perthitic. If such a felspar is metamorphosed at a temperature below the top of the solvus we can envisage several adjustments which might take place:-

a) albite will be exsolved from, or taken up by, the potassium rich host,

b) between the two resulting phases and the detrital plagioclase, which we shall assume to be present also, sodium and potassium will be exchanged until the three phases have compositions stable at the temperature at which metamorphism is proceeding. The synthetic experiments have demonstrated that three such phases can coexist during alkali exchange.

c) cooling after metamorphism will only increase the amount of free albite in the potassium felspar host.

If a bulk analysis is made of the now perthitic alkali felspar the value for Na_2O will be both a function of the temperature at which the alkali exchange took place and also of the amount of albite remaining as a perthitic intergrowth after the initial exsolution or absorption of albite from or into the host. This last mentioned variable will, in turn, be a function of the early chemical and thermal history of the detrital felspar.

The argument given under (ii) may be objected to since it applies only to a situation in which stable equilibrium between all phases has not been established. The author believes this to be an invalid criticism since similar situations may obtain in nature under sub-solvus conditions. Under sub-solvus conditions crystals made of two phases may, to some extent, behave as sub-systems within themselves and may not be in stable equilibrium with other mineral phases in the rock. Although metamorphic rocks more nearly approach stable equilibrium, during crystallization than do many igneous rocks, the rigorous application of the concept of stable equilibrium is likely to be misleading.

II Strontium Distribution Coefficients

Within the temperature limits believed to characterise high grade regional metamorphism (450-700°C?) the data on natural and synthetic felspars do not necessarily conflict. The reversal of the trend of Kd_{Srf} values, at high temperatures, has not been observed for natural felspars, this may not only be a consequence of having data for a few high grade metamorphics but also of general uncertainty concerning actual temperature ranges.

It must be remembered that for restricted composition ranges two phases can coexist in both natural alkali-felspar and in the coexisting plagioclases. As the absolute magnitudes of Kd_{Srf} values will be influenced by the relative amounts of these several phases, comparison of Kd_{Srf} values from area to area is unlikely to be as successful as comparisons within a given area. This is illustrated by D. Virgo's results.

It is readily admitted that the experimental work on strontium partitioning has associated with it too many problems concerning reaction rates and reaction mechanisms (i.e. problems of equilibrium) to provide simple and reliable calibration of the strontium geothermometer. This however has not been the main aim of the

Expt. No.	Temperature	Or. Content of Plag.
6	520°	3.52
8	660°	3.99
7	770°	8.89
11	880°	9.34
12	520°	4.37
17	650°	3.64
16	760°	10.57
29	465°	3.19
24	515°	3.69
25	650°	4.91
37	700°	12.89 (?)
26	765°	11.03
28	840°	10.89
30	520°	2.51
32	765°	3.21
21	515°	10.43
23	650°	11.53

Table 16. Showing the correlation between temperature and orthoclase content (in mol%) of the plagioclase. For full tabulation of experimental conditions see Table 8.

present investigation; but rather to confirm that strontium partitions in a temperature sensitive way and to consider a possible mechanism to explain the observations.

III <u>Potassium Content of Plagioclases</u>

Sen (1957) reported potassium analyses for a number of plagioclases separated from amphibolite facies, granulite facies and volcanic rocks. He found a trend of increasing potassium content with what would be accepted as increasing temperatures of formation. A similar trend is observable in the potassium contents of the synthetically formed plagioclases:- see Table 16. The results reported here seem to be the only experimental data available on potash in synthetic plagioclases, hence electron-microprobe studies of plagioclases crystallized from melts would be valuable.

Sen, in interpreting the trend found for natural plagioclases, considered the effects of temperature, pressure and availability of potassium. He recognized two possible important influences which <u>temperature</u> may have:-

1. Effective enlargement of the alkali sites making possible the accommodation of the larger cation

K^+. Substitution of K^+ for Na^+ will lead to strengthening of framework Si-O; Al-O bonds, because the electrostatic field strength, at the surface of the larger K^+ is smaller than for Na^+; as a result Si will be more readily able to polarize the oxygens. This will of course lead to an increase in electron density between the ions and thereby increase the covalent character of the bonds.

2. By increasing Al/Si disorder K^+ substitution is helped through meeting its coordination requirements. Disording enhances the possibility of having $Si-O_{B_1}-Al$ (or $Si-O_{B_2}-Al$) bonds rather than $Si-O_{B_1}-Si$ (or $Si-O_{B_2}-Si$) bonds, which will tend to leave O_{B_1} with a residual -ve charge thereby allowing it to be pulled closer to the alkali ion. At the same time oxygens C_1 and C_2 will move away so that the net effect will produce an environment similar to that in the usual K-felspar structure.

Pressure

The effect of increasing this variable was considered by Sen to be small, and probably not favourable to an increase in the K content of plagioclase.

Availability of Potassium

In considering this, Sen commented:- " an increased relative concentration of potassium, in an environment, will enrich the plagioclase in potassium up to a point which will be determined by the limit of solubility". The results for experiments 21 and 23, for which the closed system was potassium-rich, illustrate how a high potassium content in the environment is reflected in the high potassium content of the plagioclases. Up to the limit of incorporation of potassium this result is simply an expression of the greater statistical possibility of having a K^+ ion available, at a given instant in time, to occupy a potential cation site.

The Potassium Content of Calcium Rich Plagioclases

The results for experiments 30 and 32 indicate that an anorthite-rich plagioclase ($\underline{\Omega}$ An_{71}) will incorporate considerably less potassium than more sodic plagioclases, e.g. the plagioclases formed in experiments 24 and 26 (both $\underline{\Omega}$ 13), crystallized at similar temperatures. In addition to presenting data which reflects the same trend for natural calcium-rich plagioclases Sen discusses the underlying crystal chemistry.

The high Al:Si ratio in anorthite will mean that aluminium will tend to occupy alternate tetrahedral sites, thereby increasing the effective -ve charge for the associated oxygens (see 2nd effect of temperature).

This will allow a movement of oxygens into the alkali sites so that large cations such as K^+ will find it difficult to enter.

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APPENDIX I

The Removal of Strontium From Analytical Grade Calcium Carbonate

The method described is due essentially to P. Povandra and Z. Sulcek (1961). 2 gram portions of calcium carbonate were dissolved in dilute hydrochloric acid, after which the solution was diluted to 100ccs. This was passed through a Dowex 50-ω cation exchange column (50 mesh in a 30cm column, 1 cm diameter. Pretreatment:- 100mls 3MHCl, 50mls H_2O and 5% NH_4Cl ~~NH_4Cl~~ until neutral, finally with water until the elutrant was free of chloride ions). After washing the column with H_2O the calcium was elutriated with 0.05M diaminocyclohexanetetraaacetate (DCYTA) buffered with ammonium acetate to a pH of 5.1.

Oxalic acid was then used to precipitate a considerable portion of the calcium from the DCYTA-calcium complex. After suitable washing, the oxalate precipitate was converted, by heating at 500°C, to a carbonate with a dark carbonaceous impurity, possibly resulting from the decomposition of calcium complex not removable from the oxalate precipitate. The insoluble carbonaceous material was separated from the carbonate by filtering after the carbonate had been taken up in a minimal quantity of HCl. Pure $CaCO_3$ was then precipitated from the filtrate with ammonium carbonate. With the X-ray spectrograph, which is readily able to detect 5ppm Sr, no strontium could be detected in the calcium carbonate purified by the method described. The ion-exchange process was successfully monitored with an atomic absorption spectrograph.

APPENDIX II

Table 8

EXPT. NO	STARTING MATERIALS			CONDITIONS			PLAGIOCLASE COMPOSITION				K-FELSPAR COMP. (BULK)				K-FELSPAR COMP. ($\bar{2}01$)				DISTRIBUTION COEFFICIENTS						EXPT. NO	GROUP
	VAPOUR	K FELSPAR	PLAGIOCLASE	TEMP. °C	TIME	PRESSURE p.s.i.	Or.	Ab.	An.	Srf.	Srf.	An.	Ab.	Or.	Or.[1]	Ab.[2]	An.[2]	Srf.[2]	From bulk comp. Kd_{Srf}	Kd_{Ab}	Kd_{An}	From $\bar{2}01$ K_2O Kd_{Srf}	Kd_{Ab}	Kd_{An}		
5	5% Sr in H_2O	$Or_{80}Ab_{20}$ (mixed gels)	$An_{30}Ab_{70}$ gel	520°	3 days	17,000	7·93	66·93	22·14	2·98	6·45	1·19	21·52	70·82					2·164	·321	·053				5	A
3	"	"	"	520°	7 "	"	5·18	65·82	24·18	4·80	5·17	1·17	26·45	66·65					1·077	·402	·071				3	
4	"	"	"	520°	10 "	"	5·18	66·00	24·48	4·31	5·03	4·16	27·01	66·49					1·167	·409	·059				4	
6	·5% Sr in H_2O	"	"	520°	7 "	"	3·52	69·50	26·54	0·44	0·60	1·20	17·11	81·07					1·360	·246	·040				6	
10	"	"	"	520°	10 "	"	2·91	68·05	28·44	0·58	0·35	1·12	19·97	78·53	93·81	4·65	1·160	0·38	·603	·293	·039	·655	·068	·041	10	
8	"	"	"	660°	7 "	"	3·99	66·87	28·60	0·53	0·41	0·82	23·79	74·96	81·23	17·51	0·835	0·424	·774	·356	·029	·801	·262	·029	8	
7	"	"	"	770°	7 "	"	8·89	63·68	26·83	0·60	0·54	2·00	28·40	69·04	74·27	23·13	2·030	0·576	·900	·446	·075	·960	·363	·076	7	
9	"	"	"	850°	3 "	"	6·89	64·59	26·86	0·64	0·38	1·47	28·74	69·38	76·07	22·05	1·490	0·390	·594	·446	·053	·609	·341	·053	9	B
11	"	"	"	880°	7 "	"	9·34	63·58	26·46	0·61	0·40	1·49	27·83	70·29	69·63	28·49	1·485	0·394	·645	·437	·056	·644	·448	·056	11	
12	"	$Or_{80}Ab_{20}$ gel	"	520°	10 "	"	4·37	66·55	28·58	0·51	0·44	1·09	18·12	80·35	93·82	4·65	1·094	0·441	·866	·272	·038	·867	·070	·038	12	
17	"	"	"	650°	10 "	"	3·64	67·61	28·36	0·39	0·608	·77	23·51	75·10	82·82	15·79	·777	0·611	1·572	·347	·027	1·579	·237	·027	17	
15	"	"	"	770°	7 "	"	9·21	63·52	26·85	0·42	0·48	2·27	25·70	71·45	76·14	21·01	2·272	0·579	1·366	·404	·084	1·370	·331	·085	15	C
16	"	"	"	760°	10 "	"	10·57	64·80	24·28	0·35	0·62	1·65	30·12	67·61	74·94	22·83	1·666	0·626	1·781	·465	·068	1·799	·352	·069	16	
18	"	"	"	760°	20 "	"	8·72	66·26	24·67	0·35	0·60	1·34	28·38	69·68	76·10	21·95	1·349	0·601	1·711	·428	·054	1·718	·331	·055	18	
20	·5% Sr in 2 M alkali chloride K/Na + K = 30%	$Or_{93}Ab_7$ (mixed gels)	"	515°	10 "	"	6·65	66·28	26·42	0·65	0·31	0·86	13·17	85·66	92·19	6·63	0·866	0·311	·474	·199	·033	·475	·100	·033	20	
21	"	$Or_{98·7}$	"	515°	10 "	"	10·43	63·65	25·20	0·72	0·39	1·03	13·89	84·69	91·16	7·49	1·024	0·335	·566	·225	·042	·569	·115	·042	21	
23	"	"	"	650°	10 "	"	11·53	64·48	23·53	0·64	0·36	0·95	17·48	81·26	86·74	11·99	0·957	0·305	·475	·271	·041	·476	·186	·041	23	
29[3]	·5% Sr in H_2O	$Or_{80}Ab_{20}$ gel	$An_{15}Ab_{85}$ gel	465°	10 "	"	3·19	82·10	14·21	0·50	0·62	0·76	23·03	75·60	89·63	8·99	0·764	0·621	1·23	·280	·053	1·242	·109	·054	29[3]	
24	"	"	"	515°	10 "	"	3·69	81·40	14·53	0·39	0·52	0·73	24·39	74·35	89·34	9·39	0·739	0·528	1·33	·300	·050	1·345	·115	·051	24	
25	"	"	"	650°	10 "	"	4·91	79·98	14·71	0·40	0·62	0·83	25·70	72·85	79·19	19·36	0·838	0·618	1·52	·320	·056	1·526	·242	·057	25	
37	"	"	"	700°	10 "	"	12·89	73·90	12·89	0·49	0·60	1·95	32·26	65·19	71·49	23·96	1·952	0·604	1·21	·437	·151	1·214	·351	·151	37	
26	"	"	"	765°	10 "	"	11·03	75·62	12·86	0·50	0·51	1·02	35·72	62·75	71·43	27·04	1·021	0·513	1·03	·470	·079	1·034	·358	·079	26	
28	"	"	"	840°	10 "	"	10·89	72·79	15·65	0·66	0·49	2·12	31·18	66·30	65·01	32·47	2·038	0·485	·735	·428	·135	·734	·446	·130	28	
30	"	"	$An_{75}Ab_{25}$ gel	520°	10 "	"	2·51	25·82	71·13	0·54	0·61	1·42	21·44	76·53	89·66	8·29	1·434	0·615	1·19	·830	·020	1·14	·320	·021	30	
35	"	"	"	665°	10 "	"	3·56	24·26	71·72	0·46	0·75	1·72	16·24	81·28	81·86	15·67	1·718	0·753	1·62	·670	·024	1·62	·646	·024	35	
32	"	"	"	765°	10 "	"	3·21	28·50	67·87	0·43	0·63	1·80	20·96	76·62	87·06	10·05	1·808	0·629	1·47	·735	·03	1·48	·369	·027	32	
31	" "	" "	$An_{30}Ab_{70}$ gel	660° then 520°	for 7 " " 10 "	"	3·07	69·34	27·18	0·41	0·606	1·08	22·71	75·61	84·19	14·12	1·079	0·609	1·495	·327	·04	1·499	·204	·039	31	
34	" "	" "	"	660° then 520°	" 7 " " 20 "	"	1·87	69·51	28·21	0·41	0·62	0·88	22·77	75·72	83·35	15·14	0·885	0·627	1·53	·328	·03	1·536	·218	·031	34	
39	" "	" "	"	760° then 520°	" 7 " " 20 "	"	7·73	64·62	27·22	0·42	0·65	2·34	27·44	69·57					1·51	·425	·09				39	
38	·25% Sr in H_2O	$Or_{66·2}Ab_{31·2}An_2Srf_{0·6}$	$An_{19·4}Ab_{70·7}Or_{9·5}Srf_{0·4}$	515°	10 "	20,000	9·56	71·66	18·24	0·54	0·76	2·05	33·17	64·01					1·42	·463	·113				38	
40	·25% Sr in 1M alkali chloride	"	"	515°	10 "	"	12·85	70·71	15·90	0·54	0·72	2·36	32·18	64·73					1·34	·455	·148				40	

TABLE 8. RESULTS OF HYDROTHERMAL PARTITIONING EXPERIMENTS.

Distribution coefficients, obtained under conditions listed on the left, are given at the right hand side of the table. All compositions given in molecular percentages with Or and Ab values rounded off in the second decimal place.

Notes:-

1. Compositions determined from $d_{\bar{2}01}$.
2. Chemical values from bulk composition adjusted to fit the $d_{\bar{2}01}$ Or content.
3. The results for this experiment are unreliable since analcime appeared in the Na–Ca compartment.

APPENDIX III

Electron Microscopy

Limited opportunities to use electron microscopes in a) The C.S.I.R.O. division of soils and b) in The Department of Zoology in the University of Adelaide were taken to examine samples of a synthetic plagioclase ($H_{24}NaK$). The aims of these examinations were to discover whether or not any non-crystallized material could be recognized in either phase, and secondly to see if any peristeritic features were associated with the plagioclase. To ensure that a peristeritic texture was detectable under the conditions used to examine the synthetic plagioclase a natural peristerite served as a control. The natural material chosen was an oligoclase, with a delicate blue schiller, from Virginia U.S.A. (Adelaide University Museum No. 141).

Samples were prepared as follows. Two milligrams of material, previously ground in an agate mortar, were shaken with 5 millilitres of water (double distilled) in a small stoppered test-tube. The suspension was allowed to stand for $\frac{1}{2}$ an hour before a small portion was drawn from just beneath the surface, and placed on a carbon covered grid. After the liquid drop had been evaporated off with an infra-red lamp the specimens were ready for observation. The maximum electron accelerating potential used was 60Kilovolts.

Plates i) and ii) show samples of the alkali felspar and the plagioclase magnified 12,000x. In neither of these fields, or indeed for any other of the many fields examined, was any obviously amorphous material found. Close inspection of almost every particle examined revealed faces or cleavages. This evidence, along with the absence of bands on the powder photographs, is believed to ensure crystallization, even for these 520°C samples, was complete.

As plate iii) shows the peristeritic texture was clearly observable for the natural plagioclase, but for the synthetic plagioclase a similar fine structure was not observable. (The texture in the natural sample is very similar to that shown in photographs by Fleet and Ribbe, 1965. Although the narrow bands are dark in the fragment shown in plate iii) they are light in the image formed by the electrons on the photographic plate, and since calcium scatters electrons better than sodium, these bands probably represent anorthite rich regions).

The failure to observe peristeritic unmixing in the synthetic plagioclase formed at 520°C may reflect the fact that the temperature of formation was above the top of the peristerite solvus (Crawford, 1966, suggests the crest of the solvus lies between 450° and 500°C). It may on the other hand reflect the impossibility of differentiating, with the electron microscope, two non-intergrown phases of different composition.

Plate i) Electron micrograph showing an alkali-felspar hydrothermally crystallized from a "gel". Magnification x12,000 (x4000 by microscope, then 3x by photographic enlargement).

PLATE i)

Plate ii) Electron micrograph showing a plagioclase hydrothermally crystallized from a "gel". Magnification x12,000 (x4000 by microscope, then 3x by photographic enlargement).

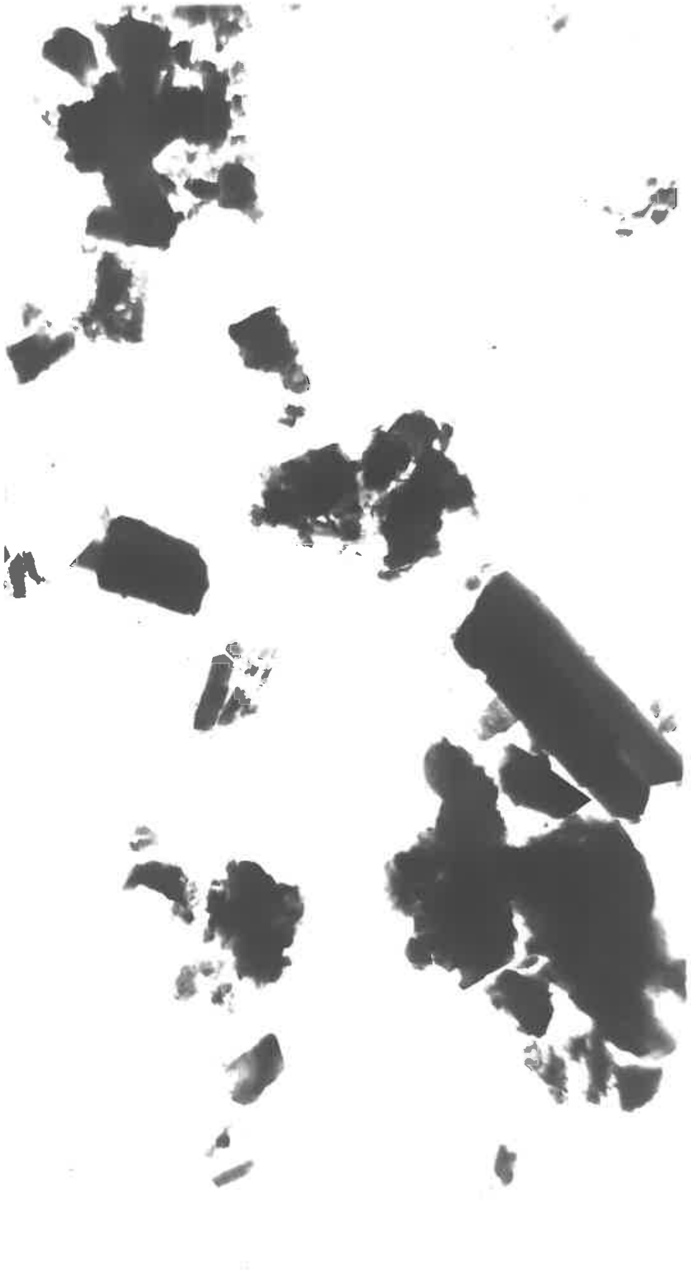

PLATE ii)

Plate iii) Electron micrograph showing the peristeritic texture observed in a fragment of oligoclase from Virginia, U.S.A. (A.U. 141). Magnification x129,000 (x43,000 by microscope, then 3x by photographic enlargement).

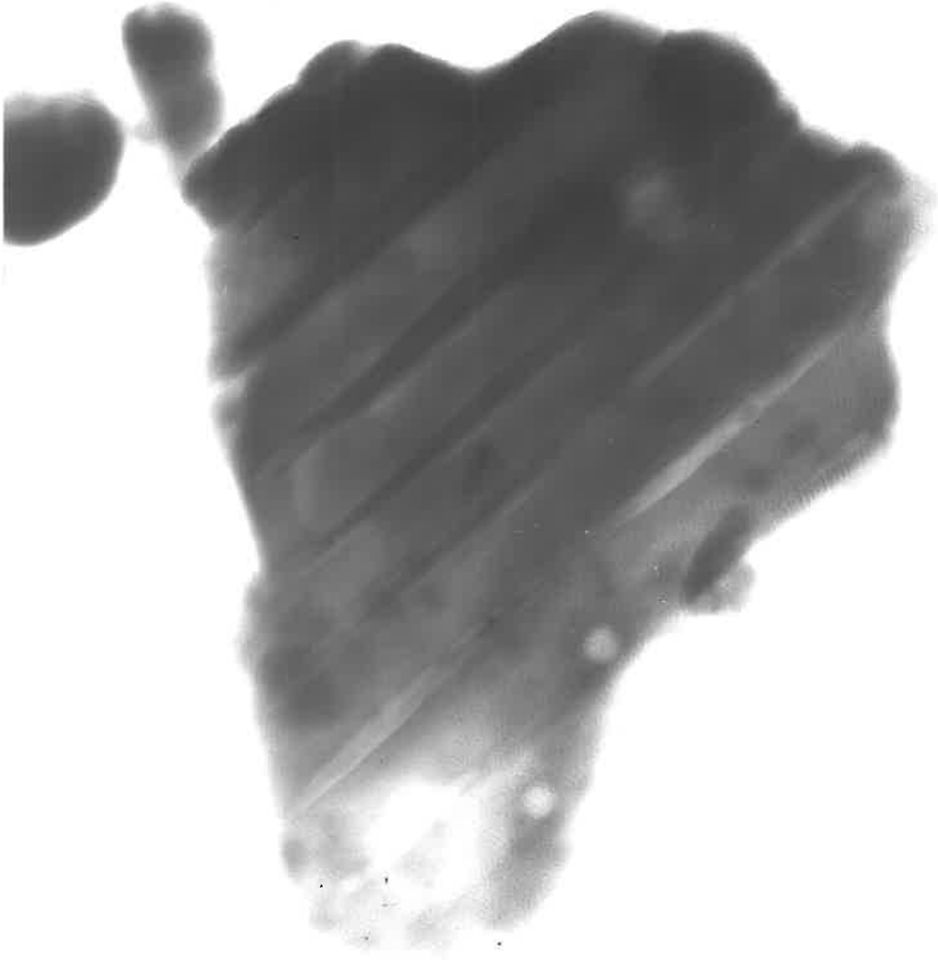

PLATE iii)

APPENDIX IV

Further Information

On White Micas

After chapter two had been prepared the work of Guidotti (1966) and Evans and Guidotti (1966) came to the author's notice.

The work of Guidotti (op. cit.) established a correlation between the basal spacing of muscovite and metamorphic grade for muscovites from sillimanite bearing schists. Evans and Guidotti (op. cit.) examined muscovites extracted from high grade pelitic schists, which spanned the sillimanite-potassium felspar isograd in Western Maine, U.S.A. They were able to show a linear correlation (at least up to 20Mol% paragonite) existed between the muscovite basal spacings and the percentage paragonite in solid solution. The following equation is given by Evans and Guidotti to represent their relationship:- $d(002)_{2M} = 10.006 - 0.27N_{p_g}$, in A°. From this equation a d(002) value for Mu_{100} is found to be 10.006A°, and for Mu_{80} to be 9.952 A°. These values lead to Co spacings of 20.0943A° and 19.9859A° respectively. The line after Evans and Guidotti (1966), drawn on fig. 8, has been positioned using these Co values. This line serves further to emphasize that the simple linear relationship between Co Mu_{100} and Co $P_{g_{100}}$, assumed by Yoder and Eugster 1955, is not strictly valid. It is also important to note that Evans and Guidotti's line, produced towards

Pg$_{100}$, will not represent the basal spacing-composition relationships displayed by the rather rare, paragonite-rich micas described by Radoslovich. The curve drawn on Fig. 8, is believed by the present author, to more accurately represent the basal spacing-composition relationships for white micas ranging in composition from Mu$_{100}$ to Pg$_{100}$. The shape of this curve seems likely to be a reflection of the non-linear relationship between average alkali-oxygen distance vs. composition determined by Burnham and Radoslovich, 1964.