WITHDRAWN
FROM
MIT LIBRARIES

A STUDY OF STRONTIUM REDISTRIBUTION
UNDER
CONTROLLED CONDITIONS OF TEMPERATURE AND PRESSURE

by

ROBERT HAROLD McNUTT
B.Sc. University of New Brunswick
(1959)

MASS. INST. TECH.
LIBRARY
LINDGREN

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY
February, 1965

Signature of Author ________________________
Department of Geology and Geophysics,
November 13, 1964

Certified by ________________________
Thesis Supervisor

Accepted by ________________________
Chairman, Departmental Committee on
Graduate Students

A STUDY OF STRONTIUM REDISTRIBUTION
UNDER
CONTROLLED CONDITIONS OF TEMPERATURE AND PRESSURE

by Robert Harold McNutt

Submitted to the Department of Geology and Geophysics on November 13, 1964, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract

Nineteen experiments involving two mineral phases and an aqueous phase, have been performed in the temperature range 450-750°C, the pressure range 3,000-15,000 psi and for time interval of 12-400 hours. These experiments were designed to study diffusion of Sr from biotite and to obtain an equilibrium distribution of Sr between mineral phases. The mineral phases which have been investigated are biotite, fluorite, albite and calcium plagioclase.

Adsorption is believed to be a cause of Sr "entering" a biotite lattice in preference to a calcium plagioclase and the reason for Sr loss from the experimental system in any one hydrothermal run.

It has been found that non-radiogenic Sr migrates from biotite at a faster rate than radiogenic Sr and the migration of both depends on the second mineral phase associated with the biotite.

It has been concluded that the major part of the non-radiogenic Sr which has left the biotites, has come from the octahedral position of the biotite or from inclusions in this mineral.

The movement of non-radiogenic Sr from biotite is believed to be the result of the dissolution of inclusions and/or associated with the changes occurring in the octahedral position in the biotite.

D/a^2 values for radiogenic Sr movement from biotite to either albite or fluorite have been determined and are found to vary from 3×10^{-9} sec^{-1} at 650°C to 8×10^{-12} sec^{-1} at 450°C. It is suggested, but not proved, that the movement at low temperatures (450-600°C) is the result of a desorption process. In the temperature range 600-750°C, the migration of radiogenic Sr could be due to volume diffusion or the result of dehydration of the biotite and/or oxidation of the Fe in the octahedral position.

An equilibrium distribution of Sr between mineral phases has not been achieved in the time alloted.

Thesis Supervisor: Harry Hughes
Title: Assistant Professor of Geophysics

Thesis Supervisor: Patrick M. Hurley
Title: Professor of Geology.

TABLE OF CONTENTS

CHAPTER II
EXPERIMENTAL PROCEDURE 76

LIST OF TABLES

Part I

Part II

LIST OF FIGURES

Part I

Part II

ACKNOWLEDGMENTS

I wish to thank Dr. Harry Hughes for his sound council and valuable suggestions concerning the experimental procedure and theoretical treatment and Professor P. M. Hurley for his constructive suggestions and comments which helped the author clarify the problem.

Professors W. H. Pinson and H. W. Fairbairn are to be thanked for their instruction in chemical, mass spectrometric and mineral separation techniques. I also wish to thank Professor W. F. Brace who helped the author in the problems of jacketing the sample and operation of the hydrothermal apparatus.

I am indebted to my fellow students R. H. Reesman, R. M. Shields, G. D. Roe and Dr. T. E. Krogh for their contributions to this study through informal discussions.

The help given by the instrument makers J. Annese, K. Harper and W. Burow is appreciated, especially the efforts of J. Annese in making the copper jackets.

My sincere appreciation is extended to my parents. Their support and encouragement during my years at M.I.T. will not be forgotten.

A special vote of thanks goes to my wife Paula. Her cheerfulness, understanding and encouragement made this thesis possible.

The financial support of the Canadian M.I.T. Trust Fund is gratefully acknowledged.

PART I

(Intended for publication)

A STUDY OF STRONTIUM REDISTRIBUTION
UNDER
CONTROLLED CONDITIONS OF TEMPERATURE AND PRESSURE

By R. H. McNutt, H. Hughes and P.M. Hurley

Abstract

Thirteen experiments were performed in the temperature range 450-750°C and the pressure range 3000-15000 psi in order to study diffusion of Sr from biotite and to see if an equilibrium distribution of Sr between minerals could be achieved. The mineral phases used were biotite, albite and fluorite.

It was found that non-radiogenic Sr migrated at a faster rate than radiogenic Sr and that the rate of migration of both depended on the second mineral phase associated with the biotite. It was concluded that the major part of the non-radiogenic Sr migrated from inclusions within the biotite or from the octahedral position of the biotite.

D/a^2 values for radiogenic Sr were found to vary from 3×10^{-9} sec^{-1} to 8×10^{-12} sec^{-1} in the temperature range 450-650°C. Low temperature migration is believed to be a desportion process, while high temperature movement could be the result of either volume diffusion or liberation during dehydration and oxidation reactions in the biotite.

It was concluded that an equilibrium distribution of Sr between mineral phases had not been realized in the times alloted.

1. Introduction.

It is well known that coexisting mineral phases from the same rock specimen give conflicting Rb-Sr ages among themselves and with the whole rock age. For example, Tilton et al (1958) found that biotites from the Baltimore gneiss gave Rb-Sr ages of 300-350 m.y. as opposed to microcline Rb-Sr and zircon Pb ages of 1100 m.y. Wetherill et al (1962) found microcline and muscovite Rb-Sr ages to agree with Pb ages at 2700 m.y., but the biotites gave consistent ages of 1800 m.y. Allsopp (1961) compared whole rock and minerals and concluded that feldspar, biotite and chlorite lost radiogenic Sr while muscovite, apatite and epidote gained it. Long (1964) found that mineral phases from a whole rock specimen which fell on a 530 m.y. isochron with a $(Sr^{87}/Sr^{86})_0$ ratio of 0.710, themselves fell on a separate isochron having an age of 390 m.y. and a $(Sr^{87}/Sr^{86})_0$ ratio of 0.782. He believes that subsequent metamorphism at 390 m.y. was intense enough to cause homogenization of Sr isotopes among minerals over a wide area.

To the authors' knowledge, the only investigation of Rb and Sr migration studied under experimental conditions is the work of Deuser (1963). For muscovite and biotite, he found that the order of leachibility was non-radiogenic Sr $>$ radiogenic Sr $>$ Rb and in going from 200-600°C the rate of loss increased greatly.

The purpose of this paper is to report findings of the redistribution of non-radiogenic and radiogenic Sr between mineral pairs under controlled conditions of temperature and pressure. The mineral phases used were biotite, fluorite and albite.

2. Experimental Procedure

Description of the Hydrothermal Apparatus and its Operation.

The experiments were performed in a stellite, cold seal pressure vessel of the Tuttle type, connected to a pressure gauge and mechanical pump by means of capillary pressure tubing. The bomb and gauge were isolated from the pump by a needle valve, which also served as a means of releasing pressure if it exceeded the desired value.

The bomb was inserted into an electrically wound furnace, heated by a regulated voltage supply. Temperature recordings at two hour intervals over a two day period showed a maximum variation of ±10°C once the plateau temperature was reached. Temperatures were measured with chromel-alumel thermocouples and recorded on a calibrated, millivolt potentiometer.

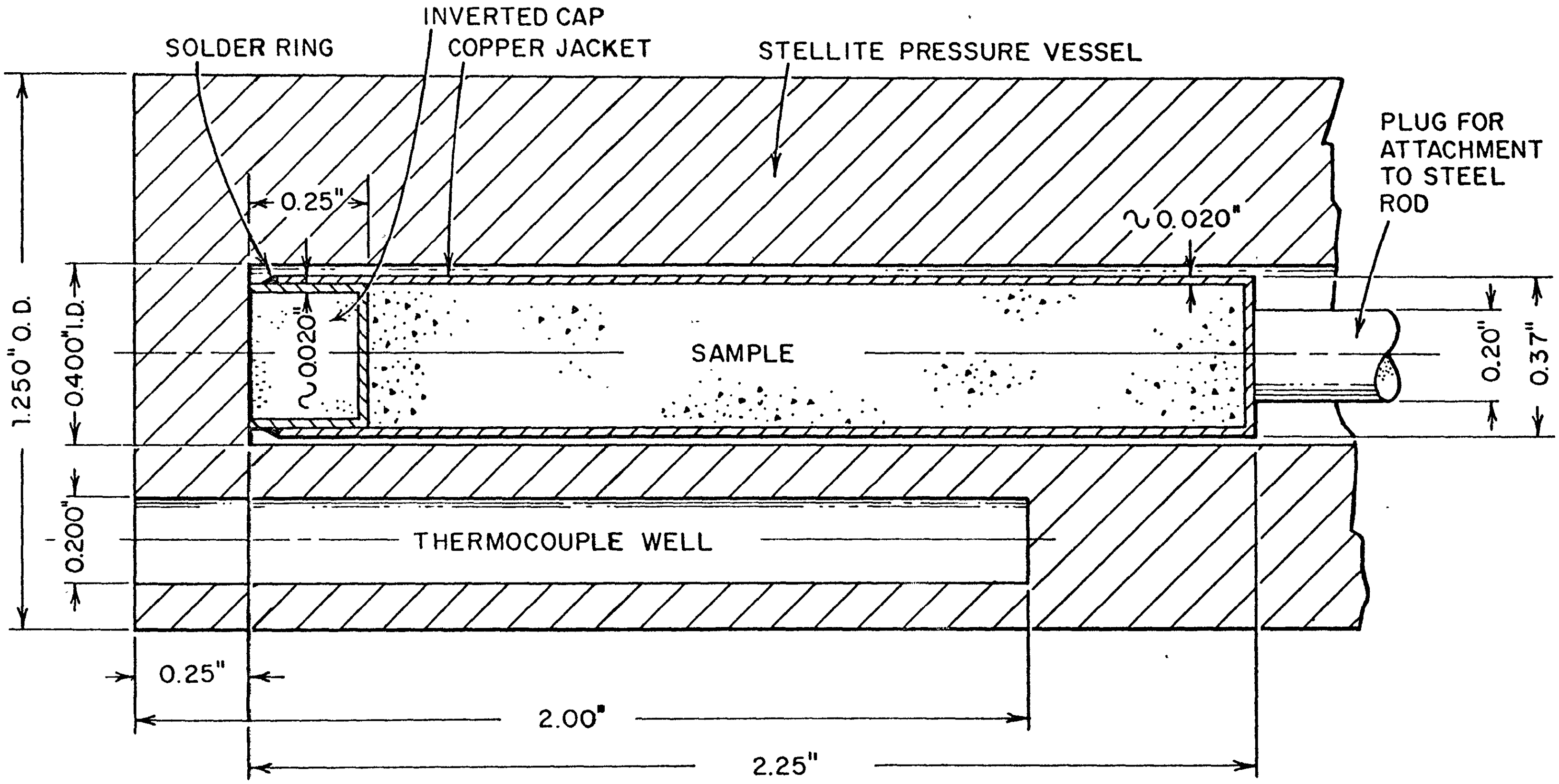
A 20°C radial thermal gradient existed between the thermocouple and the sample while a 25-30°C axial gradient existed over the length of the sample region. As the temperature intervals of the runs were 150°C, it was believed that the axial gradient could be tolerated.

The experimental system under investigation was isolated from the surroundings by use of a copper jacket.

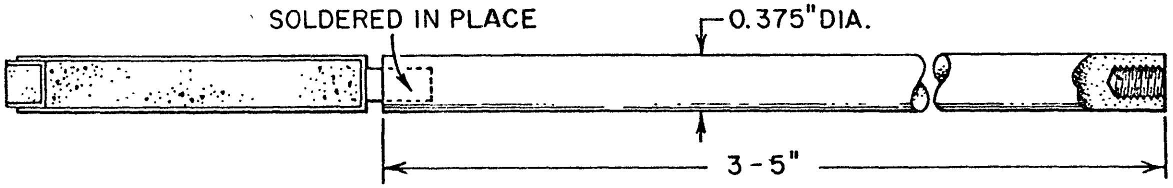
Figure 2-1 is a drawing of the jacket assembly. A of figure 2-1 shows an enlarged version of the jacket in place in the bomb, and B, the jacket assembly drawn to actual size.

The jackets were fabricated from $\frac{1}{2}$" oxygen free copper rod. At one end of the jacket a steel rod was attached which served as an aid in removing the jacket at the completion of a run and also as a filler, cutting down greatly on the volume of water needed to build up the desired pressure. A tight fitting inverted cap was pressed into place at the top of the jacket after it (the jacket) had been loaded. It was found necessary to make a narrow, shallow, axial slit on the side of the cap, so that air could escape from the jacket during the heating stage necessary for soldering. If this was not done, the cap invariably popped off, causing a partial loss of the sample.

For soldering, the assembly was immersed in a large bath of cold water until only the top $\frac{1}{2}$" of the jacket extended above the water level, (i.e. only that portion containing the cap). This kept the charge (mineral and solution) cool while heat was applied to the cap. For experimental runs at 450°C or less, it was possible to use "Easy-Flow" silver solder which melted at 1125°F and flowed at 1145°F. Runs carried out at 600-750°C needed a high temperature silver



(A) COPPER JACKET IN BOMB (3X ENLARGEMENT)



(B) COPPER JACKET AND STEEL ROD (TRUE SIZE)

FIGURE 2-1 — COPPER JACKET ASSEMBLY.

solder which both melted and flowed at 1453°F.

An experiment was performed to see if this soldering process caused any major reaction to occur. Immediately after soldering a jacket in the routine way, the jacket was opened and the contents analysed. Table 2-1 lists the results and assigning a conservative ±3% error to these values, it can be seen that no reaction occurred.

Table 2-1

Effect of Soldering on Sample from Experiment 19.

	Biotite 3138	Albite R4725	Biotite B3138 # 19	Albite R4725 #19
Total Sr	26.5 ppm	3.8 ppm	24.4 ppm	4.1 ppm

Upon completion of the run at high temperature, the bomb was quickly quenched in cold water and the jacket freed. The charge was released from the jacket by use of a tube cutter, breaking the jacket at the base and top. The mineral and liquid fell onto filter paper thus separating immediately the liquid from the minerals. About a five minute time interval was required between quenching of the bombs and breaking of the jacket. The mineral phases were washed from the filter paper, dried, separated magnetically and stored for mass spectrometric analysis.

On the average 98-95% of the original material was recovered. It was found that approximately 1% was lost on the initial recovery from the jacket, while another 2-3% was lost during magnetic separation. This loss will be mentioned again in the discussion of the analytical results.

Chemistry

The samples were dissolved in HF and HClO4, passed through cation exchange columns to separate out Sr, converted to nitrates and stored for mass spectrometer analyses. A more detailed discussion of the chemistry can be found in McNutt (1964). Early in this investigation, pyrex glass beakers and columns were used. However, Wasserburg et al (1964) demonstrated significant Sr exchange between sample and glass which would not show up in a blank analysis. Therefore, all pyrex glassware was discarded and only vycor glass columns and polyethelene and vycor beakers were subsequently used.

During the course of this investigation two Sr spikes were used. The first was a Sr^{86} spike, the details of which are presented by Pinson (1962). The second was a double spike enriched in Sr^{84} and Sr^{86}. Using this spike, isotopic fractionation corrections were made, a step not possible with a spike of single enrichment. Isotopic fractionation corrections improved the reproducibility considerably. An excellent discussion of this double spiking procedure can be found in Krogh (1964).

Contamination levels of the analytical procedure were determined by subjecting a known amount of spike Sr to the same chemistry as the samples. Table 2-2 lists the results of two blank analysis done during the course of this investigation.

Table 2-2

Blank Sr Analysis

Record Number	Sr^{86}/Sr^{88} ratio Spike	Sr^{86}/Sr^{88} ratio Blank	Sr^{84}/Sr^{88} ratio Spike	Sr^{84}/Sr^{88} ratio Blank	μgms Sr/gram
3528(S)	2.956	2.910	1.506	1.489	0.04
3767(L)	2.956	2.939	1.506	1.497	0.02

The level found is such as to be negligible, as the majority of the runs were in the neighbourhood of 20μgms Sr/gram sample.

Mass Spectrometry.

All runs were done on 6", 60° solid source, single collector mass spectrometers of the Nier type. Magnetic sweeps were used and vibrating reed electrometers amplified the ion currents. Tantalum ribbon was the filament material. The peaks were recorded on a potentiometric strip chart recorder.

Discussion of Errors

In the complex procedure from hydrothermal apparatus to mass spectrometric analysis, many sources of error are possible and hard to evaluate. Random errors which will effect the reproducibility include: variation in the bomb position in the furnace, location of the thermocouple in its well, sample weighing and its contamination, mass spectrometer instrumental fractionation, variation in rate of emission, drift in electronic components and peak height reading error. Systematic errors, which affect all runs in the same manner include: stability of the potentiometer and pressure gauge, VRE scale change and linearity of the recorder.

In the investigation only the precision error or reproducibility of measurements can be determined. Nothing can be stated about the absolute accuracy. The duplicate analyses of Sr on three mineral samples are given in Table 2-3. They were spiked with the Sr^{84}-Sr^{86} spike and corrected for machine fractionation (Krogh 1964).

Table 2-3

Summary of Duplicate Sr Analyses.

Mineral	Sr (ppm)	Average	$\bar{\sigma}$	$\bar{E}$	σ	E
Biotite 3205	30.34 29.90	30.12	±0.22	±0.73%	±0.31	±0.03%
Biotite 3138	21.16 21.42	21.29	±0.13	±0.61%	±0.18	±0.84%
Albite R4725	3.78 3.70	3.74	±0.04	±1.07%	±0.06	±1.60%

$$\sigma = \sqrt[2]{\frac{\Sigma d^2}{n-1}}, \qquad \bar{\sigma} = \sqrt[2]{\frac{\Sigma d^2}{n(n-1)}}, \qquad E = \frac{\sigma}{M} \times 100$$

Table 3 describes the precision error to be expected on a single analysis in the mass spectrometer. However the procedure in this study included the hydrothermal apparatus. One experiment was repeated in its entirety and the results are listed in Table 2-4.

Table 2-4

Summary of Sr Data for a Single Experiment Done in Duplicate.

Mineral	Sr (ppm)	Average	$\bar{\sigma}$	$\bar{E}$	σ	E
Biotite 3138	10.94 11.21	11.08	±0.13	±1.17%	±0.18	±1.61%
Albite R4725	19.71 21.25	20.48	±0.77	±3.74%	±1.09	±5.38%

$$\sigma = \sqrt[2]{\frac{\Sigma d^2}{n-1}}, \qquad \bar{\sigma} = \sqrt[2]{\frac{\Sigma d^2}{n(n-1)}}, \qquad E = \frac{\sigma}{M} \times 100$$

For the purpose of this study, an overall precision error (∇) of ±5% has been assigned to a single isotope dilution analysis.

All Sr^{87}/Sr^{86} ratio measurements were corrected for isotopic fraction assuming the Sr^{86}/Sr^{88} ratio to equal 0.1194 (Nier 1938). This gave a ∇ of ±0.02% for the corrected ratio, as seen on the results of a $SrCO_3$ Standard (Eimer and Amend, lot number 492327) run periodically over the course of time by various investigators in the geochronology laboratory at M.I.T. No duplicate isotope ratio measurements are available for the complete procedure, but in the light of results found for isotopic dilution analysis, it must be greater than ±0.02%. For the purposes of this study an arbitrary precision error (∇) of ±1% will be applied.

In conclusion, the ∇, or reproducibility of a single isotope dilution analysis in this study will be ±5%; for a single isotope ratio measurement it will be ±1%. The absolute accuracy is unknown.

3. Analytical Results

Tables 3-1, 3-2 and 3-3 list the analytical results obtained on the hydrothermal runs. Table 3-1 lists the phases used, their quantity and the temperature-pressure-time conditions of the experiment. Table 3-2 gives the Sr^{87}/Sr^{86} ratios and concentrations of the phases while table 3-3 lists the final values on the same phases at the completion of the run. The last two columns of table 3-3 show the extent of Sr migration. The minus (-) and plus (+) signs indicate Sr loss and Sr gain respectively for the mineral concerned.

All numbers are calculated on the assumption that non-radiogenic Sr has a Sr^{84}/Sr^{88} ratio = 0.0068, a $Sr^{86}/Sr^{88} = 0.1194$ and a $Sr^{87}/Sr^{86} = 0.710$. The symbol (+) indicates that the Sr^{87}/Sr^{86} ratio in question has been calculated from Sr^{84}-Sr^{86} isotope dilution analyses.

The descriptions of the minerals can be found in appendix A. Appendix B describes the method of preparation of the various aqueous solutions used in the course of this investigation.

Symbols used in this report are:

Sr^{n} = non-radiogenic Sr, with a Sr^{87}/Sr^{86} ratio of 0.710
$^{*}Sr^{87}$ = the radiogenic daughter product of Rb^{87}
N.D. = not determined
(-100, +270) etc = the mesh size of the mineral grains used in the experiment
μgms = micrograms
ppm = pacts per million
ml = milliliter

Table 3-1

Summary of Data on the Hydrothermal Experimental Runs.

Experiment Number	Components	Quantity	Temperature °C	Pressure (psi)	Time (hours)
9	Biotite 3205 (100,+270)	1.5054 grams	750	3000	97
	Fluorite (-100,+230)	0.7489 grams			
	Demin. Water	~ 0.5 ml.			
10	Biotite 3205 (-100,+270)	1.5250 grams	750	3000	210
	Fluorite (-100,+230)	0.7556 grams			
	Demin. water	~ 0.5 ml.			
12	Biotite 3205 (-100,+270)	3.0025 grams	650	8000	216
	Fluorite (-100,+230)	0.7517 grams			
	Ca-K Solution C	~ 0.5 ml			
13	Biotite 3205 (-100,+270)	1.9986 grams	650	7500	115
	Albite (-100,+200)	1.0014 grams			
	Ca-K Solution C	~ 0.5 ml			
14	Biotite 3205 (-100,+270)	1.9993 grams	650	7500	405
	Albite (-100,+200)	0.9981 grams			
	Ca-K Solution C	~ 0.5 ml.			
16	Biotite 3138 (-100,+120)	1.8993 grams	600	15000	45
	Albite (-60,+100)	0.8479 grams			
	Demin. water	0.5 ml			
17	Biotite 3138(-100,+120)	1.8984 grams	600	15000	112
	Albite (-60,+100)	0.8479 grams			
	Demin. water	~ 0.5 ml.			
18	Biotite 3138 (-100,+120)	1.8974 grams	450	7500	118
	Albite (-60,+100)	0.8479 grams			
	Demin. water	~ 0.5 ml.			

Table 3-1 continued.

Experiment Number	Components	Quantity	Temperature (°C)	Pressure (psi)	Time (hours)
20	Biotite 3138 (-100,+120) Albite (-60,+100) Demin. water	1.9003 grams 0.8510 grams ~ 0.5 ml.	450	7500	190
21	Biotite 3138 (-100,+120) Albite (-60,_100) Demin. water	1.8998 grams 0.8510 grams ~ 0.5 ml.	600	15000	12
22	Biotite 3138 (-100,+120) Albite (-60,+100) Demin. water	0.8478 grams 1.8987 grams ~ 0.5 ml.	600	15000	12
23	Biotite 3138 (-100,+120) Albite (-60,+100) K Solution D	1.9026 grams 0.8550 grams ~ 0.8 ml	600	15000	45
24	Biotite 3138A (-120,+140) K Solution E	1.9176 grams ~ 1.20 ml.	600	15000	12

Table 3-2

Summary of Data on Components used in Hydrothermal Experiments.

Component	Sr^{87}/Sr^{86}	Total Sr (ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60±0.22	4.48±0.02
Biotite 3138	3.192	26.40±0.16	5.11±0.04
Biotite 3138A	N.D.	40.09	5.35
Fluorite	0.7095	20.82±0.04	0
Albite	0.9454	3.82±0.03	0.08±0.01
Ca-K Solution C	Assumed = 0.710	0.15μgm/ml	Assumed = 0.

Table 3-3

Summary of Data on Mineral Phases at the Completion of a Hydrothermal Run.

Experiment Number	Component	Sr^{87}/Sr^{86}	Total Sr(ppm)	$*Sr^{87}$(ppm)	Sr^{n}migration (μgms)	$*Sr^{87}$ migration (μgms)
9	Biotite 3205	2.145^{+}	36.45	4.32	+1.54	-0.24
	Fluorite	0.790	24.32	0.11	+2.54	+0.08
	Water	N.D.	1.76μgms	N.D.	-	
10	Biotite 3205	2.20^{+}	31.72	4.06	-5.13	-0.64
	Fluorite	0.913	22.36	0.45	+0.83	+0.34
12	Biotite 3205	2.15^{+}	35.13	4.40	-1.15	-0.24
	Fluorite	0.714	22.15	0.01	+0.98	+0.01
13	Biotite 3205	2.64^{+}	25.85	4.12	-18.76	-0.73
	Albite	1.04	15.97	0.50	+11.75	+0.42
	Ca-K Solution C	~0.76	1.2μgms			
14	Biotite 3205	2.94^{+}	24.03	4.33	-22.84	-0.30
	Albite	1.08	16.46	0.58	+12.70	+0.50
16	Biotite 3138	5.37^{+}	16.07	5.06	-19.52	-0.10
	Albite	0.824	19.91	0.18	+13.54	+0.10
17	Biotite 3138	6.06^{+}	14.85	5.07	-21.94	-0.08
	Albite	0.842	20.00	0.23	+13.58	+0.13
	Water	0.738	~1.1μgms	N.D.		
18	Biotite 3138	5.17^{+}	16.56	5.04	-18.54	-0.14
	Albite	0.779	17.29	0.15	+11.36	+0.06

Table 3-3 continued

Experiment Number	Component	Sr^{87}/Sr^{86}	Total Sr(ppm)	*Sr^{87}(ppm)	Sr^{n} migration (μgms)	*Sr^{87}migration (μgms)
20	Biotite 3138	5.23^{+}	16.68	5.14	-18.51	+0.07
	Albite	0.781	20.02	0.14	+13.73	+0.05
21	Biotite 3138	4.93^{+}	17.32	5.09	-17.22	-0.04
	Albite	0.806	17.35	0.16	+11.44	+0.06
22	Biotite 3138	6.37^{+}	14.16	5.07	-10.34	-0.03
	Albite	0.848	7.97	0.11	+7.97	+0.06
23	Biotite 3138	5.36^{+}	16.36	5.09	-19.19	-0.04
	Albite	0.807	21.45	0.20	+14.96	+0.10
24	Biotite 3138A	N.D.	33.76	5.35	N.D.	N.D.

4. Discussion of the Data

The mineral fluorite (experiments 9, 10 and 12) shows a change from a clean, clear mineral to a gray, cloudy one. Inspection under the highest power of the petrographic microscope revealed neither minute biotite inclusions as first suspected, nor a change in the index of refraction. No explanation is put forth for this change. As a result of experiments in the temperature range 650-750°C (experiments 9, 10, 12, 13 and 14), biotite 3205 shows a marked development of black opaque material (iron oxides), a color change to a lighter brown, underlatory extinction and a partial breakdown of the grains to a finer size. These runs were performed at temperatures and total pressures (including Po_2) outside the stability limits for Fe rich biotites [Eugster (1959)]. Biotite 3138 (experiments 16-24) shows the same effect to a lesser degree. It must be concluded that the biotites have suffered partial alteration and perhaps show the beginning stages of recrystallization. The albite (cleavlandite) shows no effects of the temperature-pressure conditions to which it has been subjected.

Three features stand out when the data in table 3-3 are examined. These are: (1) that Sr from biotite migrates more readily to albite than to fluorite under the same P-T conditions (compare 12 with 13 or 14), (2) that biotite loses more Sr than albite or fluorite gains, that is, a net imbalance exists in every experiment (except 9) and (3) that Sr^n migrates more rapidly than $*Sr^{87}$.

Fluorite and albite, phases which have or can accept Ca into their structures (and therefore the geochemically similar element Sr) were chosen to be acceptor phases to take up Sr liberated from the biotites. Both plagioclase and fluorite in nature are rich in Sr, the latter mineral containing up to 10,000 ppm [Steyn (1954)]. However, on structural grounds Sr migration to these two minerals is quite different. Fluorite, CaF_2, has cubic symmetry and a face centered cubic structure with the highest possible coordination (8:4) between the Ca and F ions. Albite, $(Na, Ca)\ AlSi_3O_8$, has trigonal symmetry and a 3 dimensional tetrahedral framework structure. The cations Na^+, K^+ and Ca^{++} occur in the interstitial channelways or tunnels in this framework. As fluorite is so highly coordinated, there exists practically no interstitial space between the ions. Therefore, the only way a Sr ion could enter the lattice is in replacement of Ca, requiring the breaking of a Ca-F bond. For albite, the Sr might simply migrate into a vacant interstitial position in the lattice and become part of the structure without forcing another ion to leave.

The location of Sr^n in the biotites used in this study is not positively known, however, it is certain that $^{*}Sr^{87}$ occurs in the interlayer position of biotite in what was once a Rb site. Based on ionic size alone, Sr (ionic radius = 1.16A° in 8 fold coordination) should also occur in the interlayer position in an undisturbed biotite lattice. It is much too large to occur in the octahedral position with Fe and Mg. However, this position cannot be ruled out. There exist therefore three possibilities for the location of Sr^{n} in biotites 3205 and 3138: (1) in the interlayer position with $^{*}Sr^{87}$ (2) in the octahedral position and (3) in inclusions associated with the biotites.

If all the Sr^{n} occurs in the interlayer position, it should migrate at the same rate as $^{*}Sr^{87}$. While this is not proved, it is believed to be a good assumption, and leads to the conclusion that the major part of the Sr that has migrated has not come from the interlayer position.

If the biotites used in this study had undergone a metamorphic event sometime in their history, and as a result of this the lattice became distorted, then it is possible that Sr entered the octahedral position at this time. Changes have occurred in the octahedral position during these experiments. Fe^{+2} has oxidized to Fe^{+3} and apparently migrated out of the lattice. During this attack on the octahedral position it is possible that Sr^n migrated from the biotite to albite. This could be represented by a reaction such as:

Sr plagioclase molecule in biotite $\xrightarrow{O_2}$ Albite

In this connection, Eugster (1959) found that at a T of 600°C and a Po_2 of 10^{-19} atms or a T of 750°C and a Po_2 of 10^{-17} atms, annite broke down in the following way:

annite $\longrightarrow$ magnetite + sanidine + vapor.

The experimental systems used in this investigation have a far higher Po_2 than Eugster's system. However, it must be pointed out that formation of sanidine requires K ions from the interlayer position. This same process would liberate $*Sr^{87}$. Therefore it is necessary for the experiments biotite-albite-fluid to state that if the Sr^n is coming from the octahedral position, it is the result of a process that has not extensively affected the interlayer position in biotite.

In both biotite 3138 and 3205 inclusions were noted, the main ones being zircon, iron oxide and apatite and/or fluorite. These latter two, being Ca phases, are serious contaminants. In this connection, Jäger (1962) found a parallel correlation between the Sr content and impurity content in her biotites. Visual estimates of approximately 1% by volume have been placed on the content of inclusions in these two biotites. However, additional studies were performed on biotite 3138. These included the test for P_2O_5 as described by Shapiro and Brannock (1956) to determine the apatite content $[Ca_5(PO_4)_3(OH,F,CL)]$, X-ray fluorescence analyses of Sr in apatite and fluorite concentrates from the same hand specimen as biotite 3138, and heavy liquid separation of the inclusions using bromoform and methylene iodide. Biotite 3138 was found to contain 0.22% by weight apatite before and after an experiment (21), the apatite and fluorite both contained approximately 180 ppm Sr, and the heavy liquid treatment of the -400 mesh biotite 3138 grains reduced the Sr concentration by approximately 1.5 ppm. This means that apatite itself contributes 0.4 ppm and that all impurities together contribute 1.5 ppm. This however must be considered a minimum value for the impurity contribution of Sr to the biotite analysis. Even at -400 mesh, not all the inclusions would be freed from the biotite. These tests do show that probably the majority of the Sr^n is actually coming from the biotite lattice.

The Sr loss from the system must be connected in some way with the mineral loss during recovery and magnetic separation. The two mineral phases, biotite 3138 and albite of mesh size -100, +120 and -60, +100 respectively, taken from the same stock bottles as the samples for experiments 16-23, were weighed, mixed, separated magnetically and again weighed. They received no hydrothermal treatment. The results are given in table 4-1. They show that an excellent recovery and separation for both minerals are possible on the magnetic separator, if all grains involved are of a uniform size. But, a 3% loss on the average occurred on magnetic separation following any one hydrothermal experiment, while 1% was lost on the initial recovery from the jacket.

As the albite suffered no reduction in grain size during the hydrothermal runs and as the biotite did suffer such reduction, it is suggested that the loss on separation following a run was nearly 100% biotite and of a very small grain size.

Table 4-1

Test of Recovery from Frantz Isodynamic Magnetic Separator.

(1) Weight of biotite = 0.8971 grams

(2) Weight of albite = 0.9699 grams

(3) Thoroughly mixed together and passed through the the separator at a current of 0.36A, 15° side tilt, 25° forward tilt.

(4) Weight of biotite = 0.8957 grams

$$\text{Recovery: } \frac{0.8957}{0.8971} \text{ X } 100 = 99.84\%$$

Table 4-1 continued

(5) Weight of albite = 0.9680 grams

$$\text{Recovery: } \frac{0.9680}{0.9699} \times 100 = 99.80\%$$

In three experiments, immediately following the recovery of the minerals from the jacket and before their separation, a sample of the mixture of minerals was taken. This was analysed and compared with the results on the separated mineral fractions. The results are summarized in Table 4-2.

Table 4-2

Comparison of Total Mixture Data with Separated Mineral Data

Experiment Number	Original Sr^n in jacket (μgms)	Recovered (mineral data)	Recovered Total Mixture.
21	43.6 μgms	37.9 μgms	41.0 μgms
16	43.6 "	36.6 "	37.8 "
17	43.6 "	35.3 "	39.5 "

To obtain a representative fraction from a sample varying in grain size from -60 to ~ 250 mesh is difficult and it is not surprising that the total mixture data do not agree with the original values. The important feature to note in table 4-2 is that the total mixture values are always greater than the separated mineral values; also, with increasing time (experiment 21 to 17) the discrepancy between the separated mineral values and the original values increases. This is not the case with the total mixture values versus the original values. This again indicates that Sr is being lost from the system during magnetic separation.

Table 4-3 summarizes the data for 3 experiments concerning mineral and Sr loss. From this data and the preceding discussion, it seems that fine grained biotite, exceedingly rich in Sr, was lost on magnetic separation following a hydrothermal run.

Preliminary hydrothermal experiments /McNutt (1964)7 between a biotite, a Ca plagioclase (An_{50-60}) and a Sr solution, showed that Sr from the fluid phase preferred biotite to Ca plagioclase, a "sink" phase for Sr. Also Deuser (1963) commented on the fact that the high temperature distribution of Sr between fluid and mineral returned to STP conditions in minutes when the charge was quenched following a run. These observations might indicate that Sr simply adsorbed back onto the mica surface during the quench, and may or may not have returned into the lattice.

Applying this to the system biotite 3138-albite-water it is suggested that the Sr contained in the fluid phase at high temperature adsorbed back onto the grain surface during the quenching process. Because of the much greater surface area of biotite in comparison with albite, the major part of the Sr would adsorb

Table 4-3

Balance of Sr in Hydrothermal Runs.

A. Mineral Recovery:	21	16	17
(1) Original amount of minerals in Cu jacket	2.7508 grams	2.7472 grams	2.7463 grams
(2) Initial recovery of minerals from jacket	2.7165 "	2.6753 "	2.7093 "
(3) Separated portion for "total mixture" analysis	0.1571 "	0.0980 "	0.0990 "
(4) Final recovery of biotite from Frantz	1.7195 from orig 1.8998	1.7184 from orig 1.8993	1.6238 from orig 1.8984
(5) Final recovery of albite from Frantz	0.7859 from orig 0.8510	0.7735 from orig 0.8479	0.7901 from orig 0.8479
(6) Lost on separation on Frantz	0.0540 grams	0.0254 grams	0.1884 grams
(7) Total loss	0.0883 = 3.2%	0.0973 = 3.5%	0.2334 = 8.5%

Table 4-3 - continued

B. Strontium Recovery

	21	16	17
(1) Original quantity	$\frac{43.6\ \mu\text{gms}}{2.7508\ \text{grams}} = 15.8\text{ppm}$	$\frac{43.6\ \mu\text{gms}}{2.7472\ \text{grams}} = 15.9\text{ppm}$	$\frac{43.6\ \mu\text{gms}}{2.7463\ \text{grams}} = 15.9\text{ppm}$
(2) Total mixture	$\frac{2.3\ \mu\text{gms}}{.1571\ \text{grams}} = 14.9\text{ppm}$	$\frac{1.4\ \mu\text{gms}}{.0980\text{grams}} = 13.8\text{ppm}$	$\frac{1.4\ \mu\text{gms}}{.0990\text{grams}} = 14.4\text{ppm}$
(3) Biotite	$\frac{21.0\ \mu\text{gms}}{1.7195\ \text{grams}} = 12.2\ \text{ppm}$	$\frac{18.8\ \mu\text{gms}}{1.7184\text{grams}} = 10.9\text{ppm}$	$\frac{15.9\ \mu\text{gms}}{1.6238\text{grams}} = 9.8\text{ppm}$
(4) Albite	$\frac{13.5\ \mu\text{gms}}{.7859\text{grams}} = 17.2\text{ppm}$	$\frac{15.2\ \mu\text{gms}}{1.7735\text{grams}} = 19.7\text{ppm}$	$\frac{15.6\ \mu\text{gms}}{.7901\text{grams}} = 19.8\text{ppm}$
(5) Unaccounted for	$\frac{6.8\ \mu\text{gms}}{0.0883\text{grams}} = 77.6\text{ppm}$	$\frac{8.2\ \mu\text{gms}}{0.0973\text{grams}} = 84.3\text{ppm}$	$\frac{10.7\ \mu\text{gms}}{.2334\text{grams}} = 45.8\text{ppm}$

back onto the biotite grains. In addition, the biotite has with time further increased its surface area by partial breakdown. These small grains with their very large surface area would adsorb Sr in a disproportionate amount with respect to their weight contribution to the whole biotite sample. This will explain why the discrepancy between mineral values and the original values (table 4-2) increases with time.

The purpose of the Ca^{++}-K^{+} solution in experiments 12, 13 and 14 and of the K^{+} solutions in 23 and 24 (see appendix B for description of the solutions) was to affect an ion exchange reaction between K^{+} and Ca^{++} in the solution with $*Sr^{87}$ in the interlayer position of the biotite. The K^{+} ions in experiment 23 and 24 did not exchange with $*Sr^{87}$ in biotite 3138. The Ca^{++}-K^{+} solution may or may not have done so in biotite 3205. $*Sr^{87}$ has been lost in these experiments, but it may be a temperature effect and independent of the presence of Ca^{++} and K^{+} in the solution. This was not pursued any further, but a study of this sort should prove profitable especially in the light of the work done by Kulp and Engel (1962) and Gerling and Ovchinnikova (1962), where these authors found that the Rb/Sr ratios could be altered by exchange reactions between ions in a liquid phase and those of the interlayer position of biotite.

Figures 4-1 to 4-6 show graphically the data for experiments 16, 17, 18 20 and 21. With these experiments, an attempt was made to reach an equilibrium distribution of Sr between biotite and albite at a particular T and P. Using the albite data (figure 4-1), it appears that Sr^n has reached an equilibrium value, but the biotite data for the same T-P conditions do not show this (figure 4-2); also $*Sr^{87}$ continued to migrate to albite after the Sr^n has ceased (figure 4-3). If a true equilibrium situation prevailed at 600°C, $*Sr^{87}$ also would have ceased to migrate after 45 hours (experiment 16) because once the $*Sr^{87}$ ion left biotite it would enter albite in the same manner as Sr^n. The apparent picture of Sr equilibrium (figure 4-1) probably represents Sr^n having been drained from a site other than the interlayer position, and that although both Sr^n and $*Sr^{87}$ continued to migrate after 45 hours, their quantity was so low that no appreciable change in concentration was noted. Therefore, it is concluded, but not proved, that equilibrium has not been reached in the time alloted due to kinetic effects.

5. Diffusion of $*Sr^{87}$

The study of diffusion is based on Ficks Law. It can be stated in two ways:

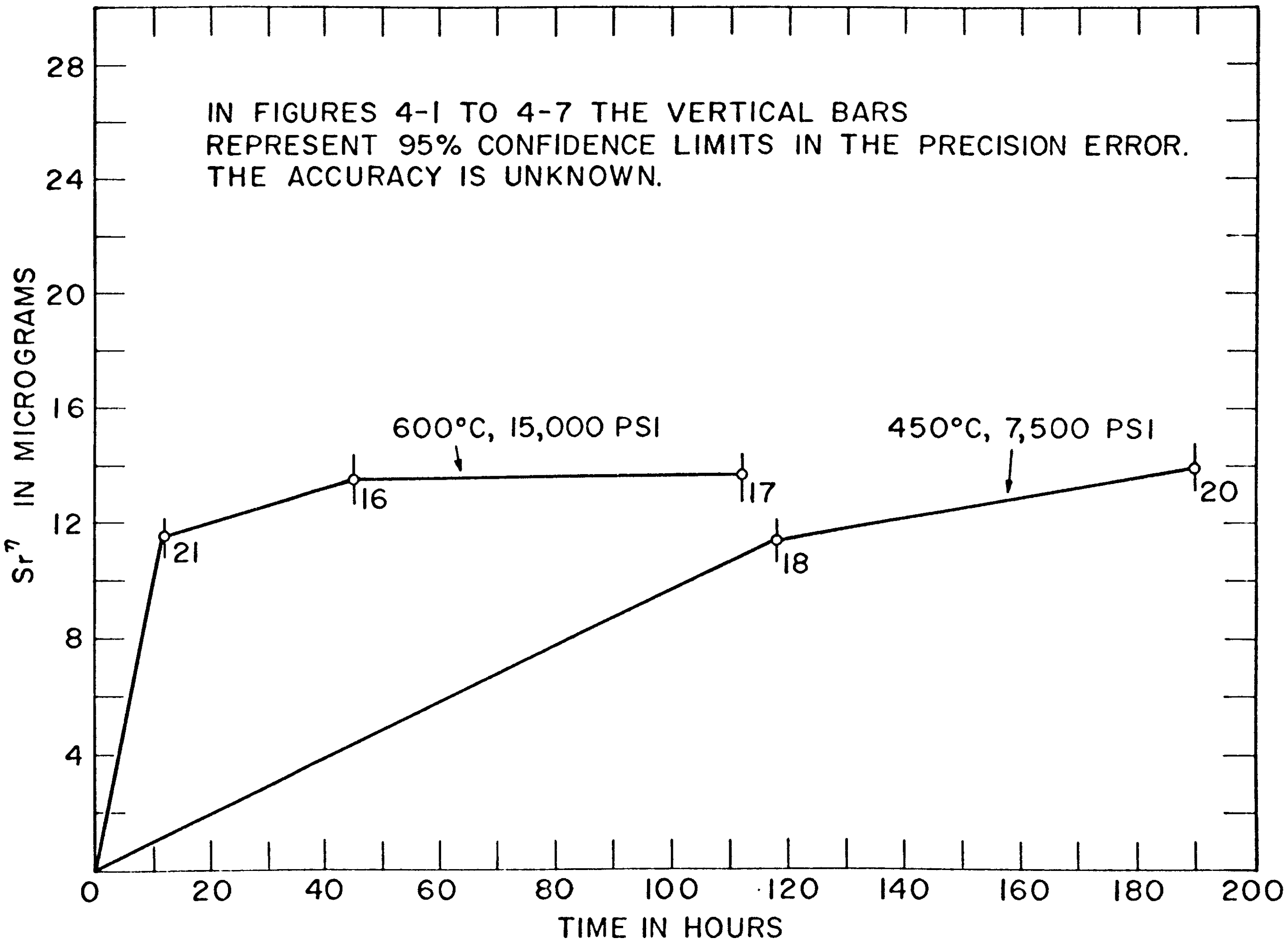


FIGURE 4-1 MOVEMENT OF Sr^{7} FROM BIOTITE 3138 TO ALBITE USING THE ALBITE DATA

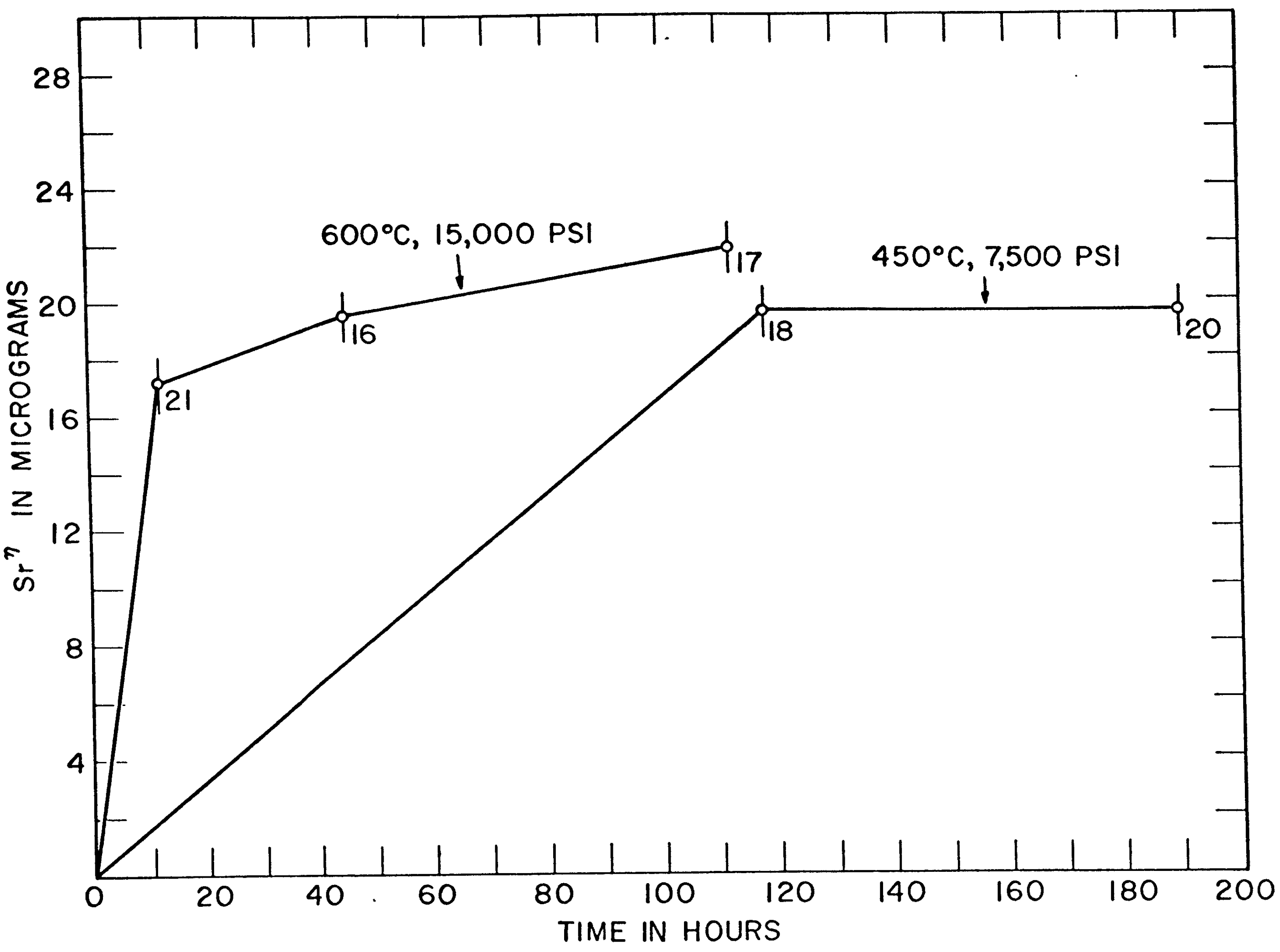


FIGURE 4-2 MOVEMENT OF Sr^{87} FROM BIOTITE 3138 TO ALBITE USING THE BIOTITE DATA

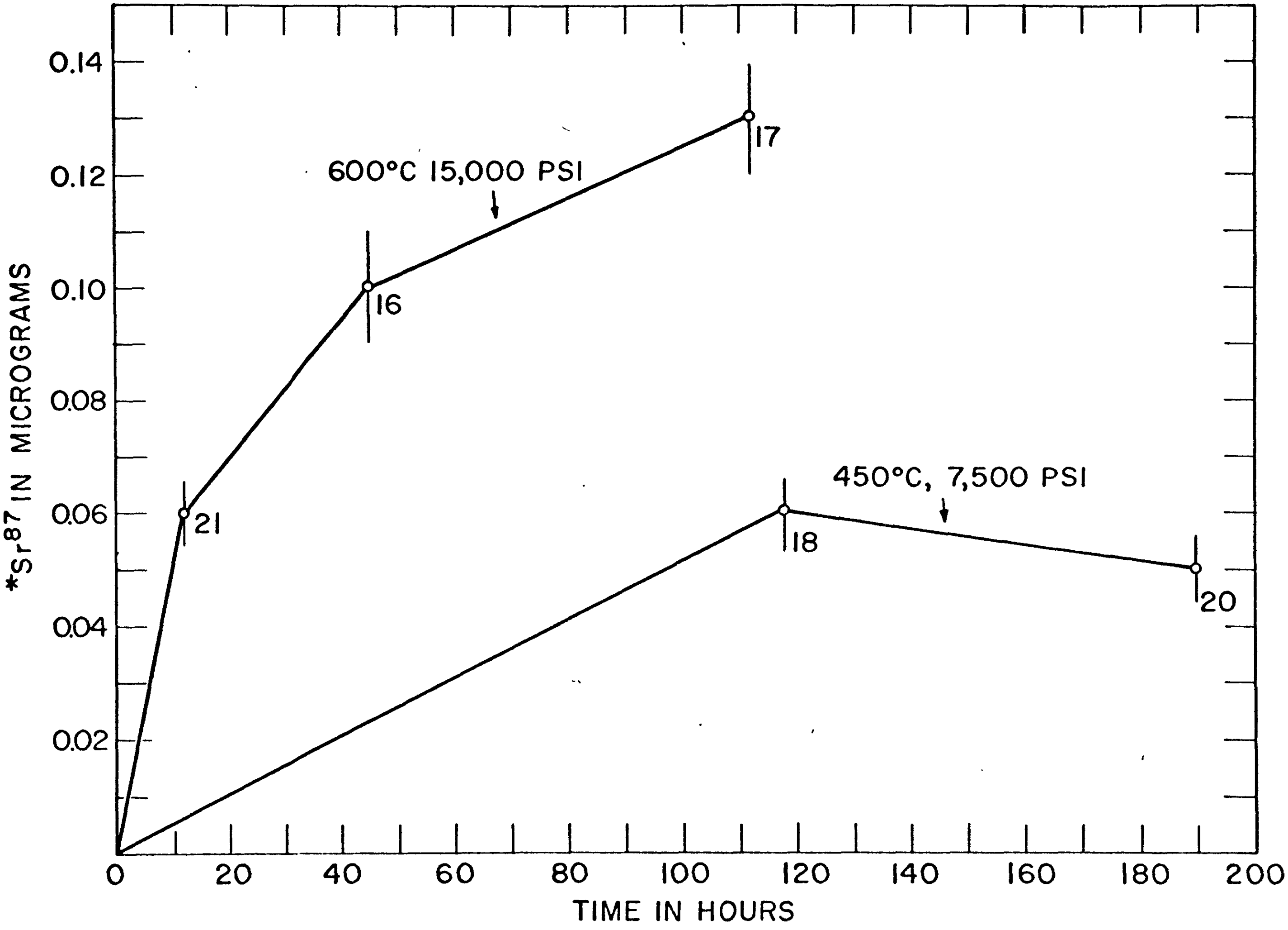


FIGURE 4-3 MOVEMENT OF *Sr^{87} FROM BIOTITE 3138 TO ALBITE USING THE ALBITE DATA

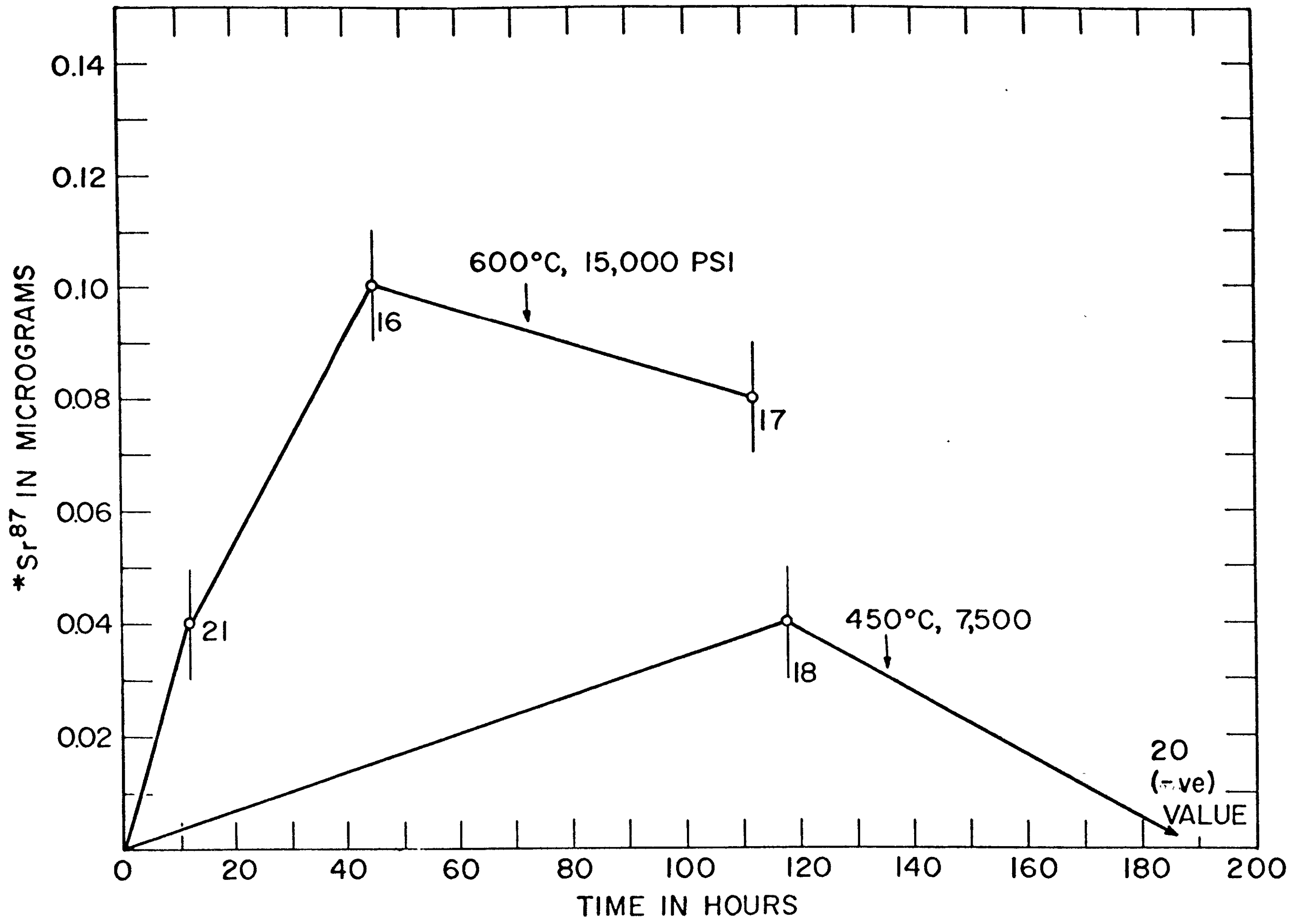


FIGURE 4-4 MOVEMENT OF $^*Sr^{87}$ FROM BIOTITE 3138 TO ALBITE USING THE BIOTITE DATA

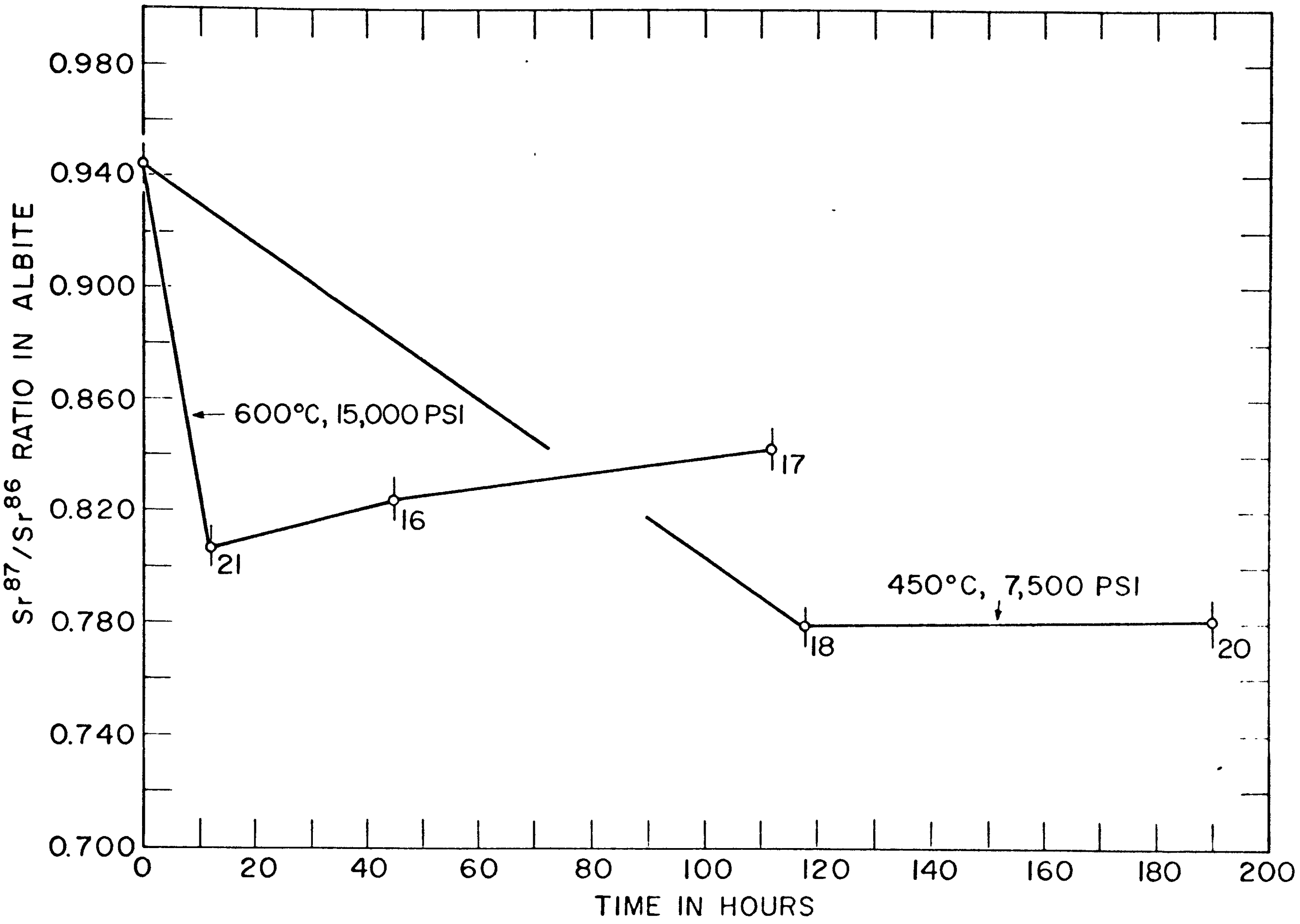


FIGURE 4-5 THE CHANGE IN THE Sr^{87}/Sr^{86} RATIO IN ALBITE WITH TIME

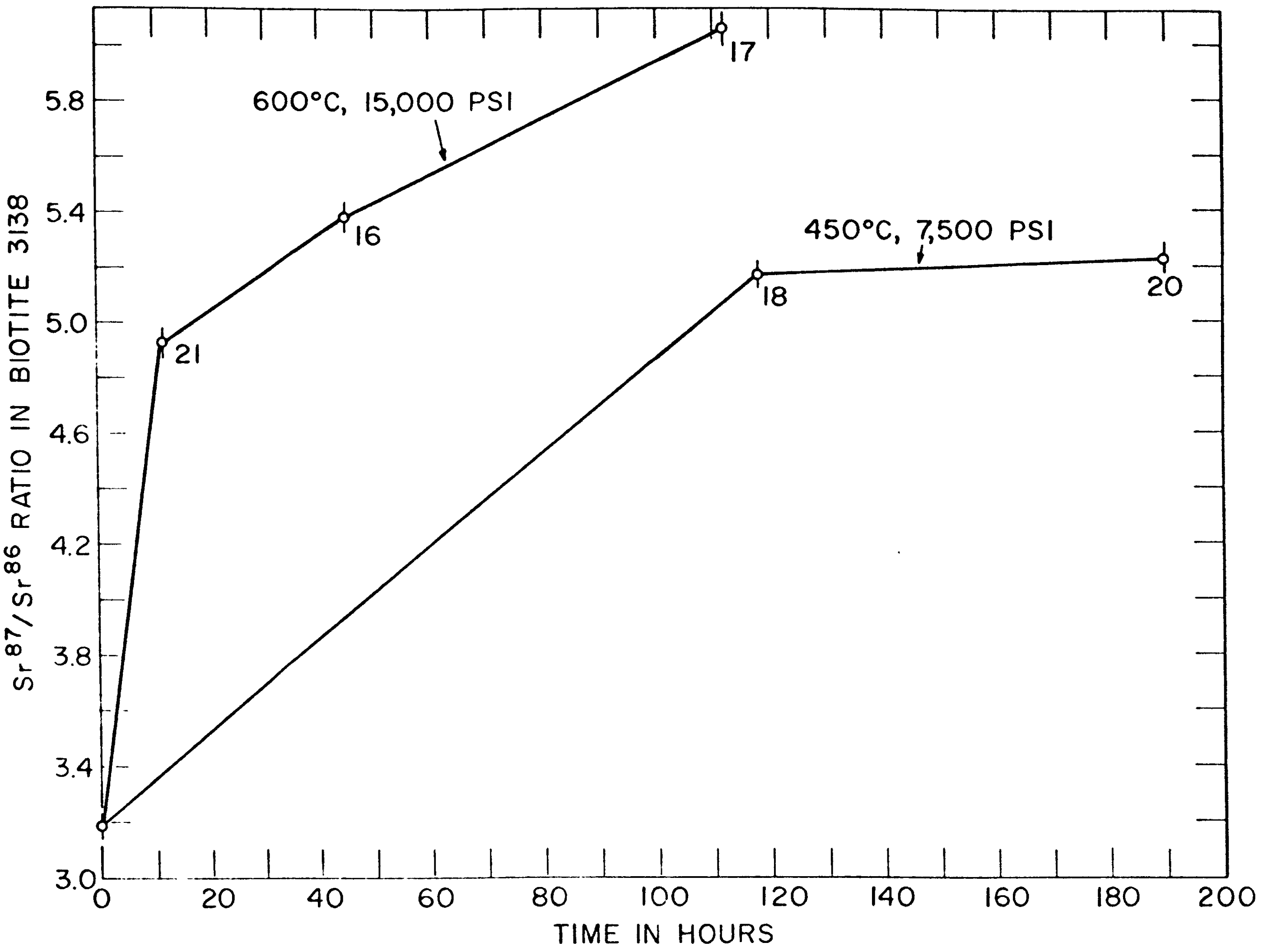


FIGURE 4-6 THE CHANGE IN THE Sr^{87}/Sr^{86} RATIO IN BIOTITE 3138 WITH TIME

$$P = -D \frac{\partial c}{\partial x} \qquad (1)$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (2)$$

Equation (1) gives the flux P in the steady state of flow through a unit cross section area, in terms of the concentration gradient and a constant D, the diffusion coefficient. Equation (2) refers to the non stationary state of flow. It describes the accumulation of matter at a given point in a medium as a function of time. This latter form is easily applied to various diffusion models.

If a homogeneous phase of uniform initial concentration and uniform concentration at the surface is assumed, then it is possible to obtain solutions to Ficks' Law for a sphere, cylinder, and slab (Carslaw and Jaeger, 1958, Barrer, 1941). These solutions are further simplified if the surface concentration is taken equal to zero. The most convenient way to express the equations is in terms of F, the fraction lost from the mineral at anytime t.

(1) Slab - this applies to an infinite slab or a slab with impermeable edges.

$$F = 1 - \frac{8}{\pi^2} \sum_{N_{odd}} \frac{1}{n^2} \exp\left[\frac{-n^2\pi^2 Dt}{4\ell^2}\right]$$

where ℓ = half thickness of the slab. For $F < 0.03$ this series can be approximated by:

$$\frac{D}{\ell^2} \simeq \frac{7.76\, F^2}{\pi^2 t}$$

(2) Cylinder - this refers to a cylinder of infinite lenth or with finite length having impermeable ends:

$$F = 1 - \sum_{1}^{\infty} \frac{4}{\mu_o^{2}} \exp\left[\frac{\mu_o^{2} Dt}{a^2}\right]$$

where a is the radius of the cylinder and μ_o are the roots of the Bessel function of the first kind and zero order. For $F < 0.02$, this can be approximated by:

$$\frac{D}{a^2} \simeq \frac{1.945F^2}{\pi^2 t}$$

(3) Sphere

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2\pi^2 Dt}{a^2}\right)$$

where a is the radius of the sphere. If F is small (< 0.10) this can be approximated by (Gerling and Morozova 1962):

$$F = \frac{6}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2} t\right)^{\frac{1}{2}} - \frac{3Dt}{a^2}$$

if $F < 0.01$ it can be further approximated to:

$$\frac{D}{a^2} \simeq \frac{0.862F^2}{\pi^2 t}$$

Using these three models and the assumption of zero surface concentration, the D/a^2 values for $*Sr^{87}$ have been calculated for experiments 9-21. The results are listed in table 4-4.

The values as calculated are for the specific systems biotite-albite and biotite-fluorite. They are not considered to represent D/a^2 values for $*Sr^{87}$ diffusion from biotite for any system except the ones investigated during the course of this study. The reason for this is obvious from the preceding discussion on Sr behaviour towards albite and fluorite.

Table 4-4

Values of D/a^2 for $*Sr^{87}$ (in 10^{-10} sec^{-1}) using Three Models

Biotite 3138 in Experiment:	Slab	Cylinder	Sphere
21	7.0	1.7	0.76
16	5.0	1.3	0.58
17	3.5	0.9	0.23
18	0.7	0.16	0.08
20	0.3	0.08	0.03
Biotite 3205 in Experiment:			
9	32	8.1	4.5
10	91.0	23.0	11.0
13	120	31.0	14.0
14	16	4.1	1.8
12		0.8	

Table 4-4 continued

At 600°C (21, 16, 17): Average Slab = 5.2×10^{-10} sec^{-1}
" Cylinder = 1.3×10^{-10} sec^{-1}
" Sphere = 0.5×10^{-10} sec^{-1}
At 450°C (18, 20) " Slab = 0.5×10^{-10} sec^{-1}
" Cylinder = 0.12×10^{-10} sec^{-1}
" Sphere = 0.05×10^{-10} sec^{-1}

A precision error of ± 30% is placed on these numbers. This is equal to 2σ or 95% confidence limits. The absolute accuracy is unknown.

The diffusion coefficient D itself cannot be determined, because the diffusion radius is unknown. The radius of the biotite grain itself is known, but this is not necessarily equal to the diffusion radius. The Sr ion may only have moved a few microns in distance before it reached the grain surface or a lattice imperfection and thus readily escaped. Therefore, it is necessary to deal with D/a^2.

The activation energy involved in the diffusion of $*Sr^{87}$ can be determined by use of the Arrenhius equation:

$$\frac{D}{a^2} = \frac{D_o}{a^2} e \; - \frac{E_{act}}{RT}$$

where a = diffusion radius

$\frac{D_o}{a^2}$ = a constant, the frequency factor

E_{act} = the activation energy in calories/mole

R = the gas constant = 1.987 calories/mole-degree

T = the temperature in degrees Kelvin

By plotting $\log_{10} D/a^2$ versus $1/T$, the E_{act} is determined from the slope of the line (equal to $-\frac{E_{act}}{2.303R}$). The data in Table 4-4 have been treated in this way and the results are seen in figure 4-7.

On the basis that Sr^n in the biotite and albite have Sr^{87}/Sr^{86} ratios of 0.710, the E_{act} for the diffusion of $*Sr^{87}$ from biotite 3138 to albite is 20 Kcal/mole in the temperature range 600°-450°C. This calculation is based on the cylindrical model, believed to be the best approximation to biotite.

A line is seen connecting the data for 650°C with that for 600°C. It must be remembered that two different biotites are involved here, biotite 3205 at 650°C and biotite 3138 at 600°C. However, if the discussion is restricted to the migration of $*Sr^{87}$ from the biotite interlayer position, then it is believed that these two biotites can be considered as one. Looking at figure 4-7 it is seen that a much higher E_{act} of 84 Kcal/mole exists between 650°-600°C than in the temperature range 600-450°C. An E_{act} of 60 Kcal/mole is found for the system biotite 3205 - fluorite in the temperature range 750-650°C. The E_{act} for this

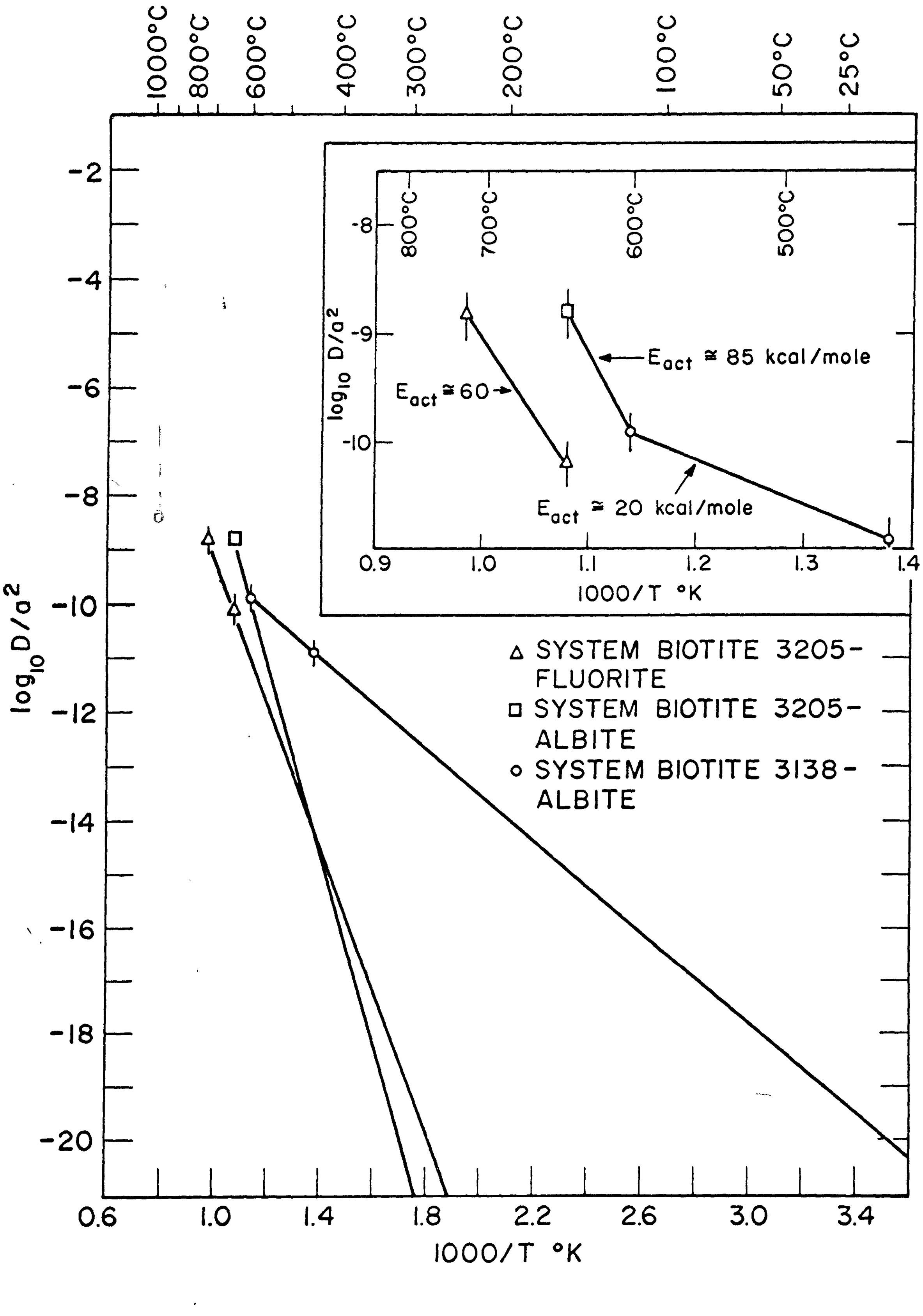


FIGURE 4-7 LOG$_{10}$ D/a^2 vs 1000/T °K

system is less in value than that for migration at 650-600°C. However, notice that the D/a^2 value for $*Sr^{87}$ diffusion from biotite 3205 to fluorite is the same at 750°C as the D/a^2 for biotite 3205 to albite at 650°C. This is compatible with what was concluded earlier. That is, Sr migrates at a faster rate to albite than to fluorite.

By knowing the E_{act} values it is now possible to determine the time-temperature-D/a^2 relationships as they might apply in geological circumstances. For example, in table 4-5 the temperatures required for 2% loss and 50% of $*Sr^{87}$ from biotite in 1 m.y., 100 m.y., and 1 b.y. are listed. The values given are calculated on the basis of volume diffusion, using the cylindrical model and with the E_{act} values of 20, 60, and 84 Kcal/mole.

As the ratio of 0.710 is assumed for Sr^n in these biotites, the D/a^2 values calculated here must represent maximum values, i.e. minimum E_{act} values, to be found in the experimental systems. If the value of 20 Kcal/mole for E_{act} is applied to temperature-time conditions in the earth, it is seen that significant $*Sr^{87}$ loss from biotite could occur over geologic time without the help of a thermal event at some time subsequent to the mineral's formation. For example, in 1 b.y. at a temperature of 60°C, 50% of the $*Sr^{87}$ could be lost

Table 4-5

Temperature at which 50% and 2% of *Sr^{87} would be lost from Biotite in times of one million, one hundred million and one billion years

E_{act} (Kcal/mole)	2% loss of *Sr^{87}			50% loss of *Sr^{87}		
	1 m.y.	100 m.y.	1 b.y.	1 m.y.	100 m.y.	1 b.y.
(1) 20	80°C	25°C	-	170°C	95°C	60°C
(2) 60	340°C	290°C	265°C	430°C	360°C	335°C
(3) 85	360°C	320°C	300°C	430°C	375°C	360°C

(1) Corresponds to the experimental system biotite 3138-albite in the temperature range 600-450°C.

(2) Corresponds to the experimental system biotite 3205-fluorite in the temperature range 750-650°C.

(3) Corresponds to the experimental system biotite 3205-albite in the temperature range 650-600°C.

from biotite. This implies that all Precambrian biotite should show significant $*Sr^{87}$ loss. However, the data for the systems biotite 3205-albite and biotite 3205-fluorite suggest that a thermal event is indeed needed for any significant $*Sr^{87}$ migration to occur. The incompatability of these latter results with the system biotite 3138-albite necessitates a further look at the cause of $*Sr^{87}$ loss from biotite in the temperature range 600-450°C.

Looking at figure 4-3, it appears that the movement of $*Sr^{87}$ is reaching a "plateau" value in the region of 0.15-0.20 μgms. For the same reasons as presented earlier, this is not considered an approach to an equilibrium value. It is suggested, but not proved, that this approach to a plateau value represents drainage or desorption of $*Sr^{87}$ from the grain surfaces, grain imperfections or some crystal defect. This would correspond to the low temperature loss of Ar from mica as found by Amirkhanov et al (1959a, 1959b) and Fechtig et al (1960). If this value of 0.15 to 0.20 μgms is correct, then approximately 2% of the $*Sr^{87}$ in biotite 3138 is residing in locations other than the interlayer position of the biotite.

The D/a^2-temperature-time conditions as derived from the data in the temperature range 750-600°C (the systems biotite 3205-fluorite and biotite 3205-albite) are compatible with conditions expected in nature. For example, 50% of the $*Sr^{87}$ could be lost from the biotite in 1 m.y. at a temperature of 430°C, a temperature certainly within the metamorphic range.

One point must be made here which concerns the pressure conditions of the experimental runs (9 to 17 and 21) in the temperature range 600-750°C. The runs at 600°C and 1000 bars pressure (biotite 3138) are within the stability limits of biotite except for the high Po_2 which causes oxidation as noted. At 650°C and 500 bars it is marginal and at 750°C and 200 bars it is outside the stability limits. That is, at these higher temperatures and low total pressure biotite (either 3138 or 3205) should start to lose its structural water. There does exist therefore the strong possibility that the $*Sr^{87}$ being released at high temperature is due in large part to the breakdown of the interlayer position of the biotite. In this connection, Gerling and Morozova (1957) and Saradov (1961) believe that the loss of Ar from the interlayer position in micas will only come about when the mica begins to break down by giving off its structural water. Also Gerling et al (1963) found that the higher the Fe^{+3}/Fe^{+2} ratio in biotites the lower the E_{act} for the release of Ar. They conclude that the entry of Fe^{+3} into the structure somehow "loosens" it up and makes diffusion easier. In this present study, Fe certainly was oxidized during the hydrothermal runs, and this too may have aided in $*Sr^{87}$ escaping from the biotite.

6. Summary and Conclusions

The adsorption of Sr onto the mica surface, coupled with the loss of the fine sized mica flakes, is believed to be the cause of the Sr loss noted in any one experiment.

Sr^n that migrated from biotite to albite or fluorite came primarily from inclusions within biotite grain and/or from the octahedral position of the biotite. This migration of Sr^n is believed not to be diffusion controlled, but instead is somehow associated with the dissolution of impurities or with the changes occurring in the octahedral position in the biotite.

D/a^2 values for $*Sr^{87}$ movement from biotite to albite or fluorite vary from 3×10^{-9} sec^{-1} at 650°C to 8×10^{-12} sec^{-1} at 450°C using the relationships of volume diffusion. It is suggested that $*Sr^{87}$ migration in the temperature range 600-450°C is due to a desorption process. Migration at 600-750°C can be the result of dehydration and oxidation reactions in the biotite, but the experimental data found at high temperature are compatible with the idea of $*Sr^{87}$ loss from biotite due to volume diffusion during a thermal event. All D/a^2 values are calculated on the assumption that the

Sr^{87}/Sr^{86} ratio of Sr^n is 0.710.

The movement of Sr^n and $*Sr^{87}$ from biotite depends upon the nature of the mineral phase in association with the biotite.

Acknowledgments

We thank the assistance given us by Professors H. W. Fairbairn and W. H. Pinson who aided the authors in mineral separation, chemical processing and mass spectrometry. The support of the Division of Research of the Atomic Energy Commission is gratefully acknowledged.

References

Allsopp H. L. (1961) Rb-Sr age measurements on total rock and separated mineral fractions from the old granite of the Central Transvaal. J. Geophy. Res. 66, 1499-1507.

Amirkhanov K. I.,Bartnitskii E. N., Brandt S. B. and Voitkevich G. V. (1959a) The migration of argon and helium in certain rocks and minerals. Doklady Ac. Sci. U.S.S.R. 126, 394-395.

Amirkhanov K. I., Brandt S. D. and Bartnitskii E. N. (1959b) The diffusion of radiogenic argon in feldspars. Doklady Ac. Sci. U.S.S.R. 125, 210-212.

Barrer R. M. (1941) Diffusion In and Through Solids Macmillan Co. London.

Carslaw H. S. and Jaeger J. C. (1947) Conduction of Heat in Solids. Oxford Univ. Press, London.

Deuser W. G. (1963) The effect of temperature and water pressure on the apparent Rb-Sr age of micas. Phd. Thesis, Penn. State Univ.

Eugster H. P. (1959) Reduction and oxidation in metamorphism. Researches in Geochemistry 397-426 John Wiley & Sons, New York.

Fechtig H, Gentner W. and Zahringer J. (1960) Argonbestimmungen an Kaliummineralien - VII Diffusionsverluste von argon in mineralien und ihre Aswirkung auf die kalium-argon-altersbestimmung. Geochim. et Cosmochim. Acta. 19, 70-19.

Gerling E. K., Levskii L. K. and Morozova I. M. (1963) On the diffusion of radiogenic argon from minerals. Geochemistry 6, 551-555.

Gerling E. K. and Morozova I. M. (1957) Determination of activation energy of argon liberated from micas. Geochemistry 4, 359-367.

Gerling E. K. and Morozova I. M. (1962) Determination of the activation energy for the release of argon and helium from minerals. Geochemistry 12, 1255-1268.

Gerling E. K. and Ovchinnikova G. V. (1962) Cause of low age values determined on micas by the Rb-Sr method. Geochemistry 9, 865-875.

Jäger E. (1962) Rb-Sr age determination on micas and total rocks from the alps. J. Geophy. Res. 67, 5293-5306.

Krogh T. E. (1964) Strontium isotopic variation and whole rock isochron studies in the Grenville Province of Ontario. 12th Annual Progress Report for 1964, U.S.A.E.C. Contract AT (30-1)-1381.

Kulp J. and Engles J. (1962) Discordances in K-Ar and Rb-Sr isotopic ages. Radioactive Dating, International Atomic Energy Agency, Vienna, 219-238.

Long L. E. (1964) Rb-Sr chronology of the Carn Chuinneag intrusion, Ross-shire, Scotland. J. Geophy. Res. 69, 1589-1597.

McNutt R. H. (1964) A study of Sr redistribution under controlled conditions of temperature and pressure. 12th Annual Progress Report for 1964, U.S.A.E.C. Contract AT(30-1)-1381.

Nier A. O. (1938) Isotopic constitution of Sr, Ba, Bi, Tl and Hg. Phys. Rev. 54, 275-278.

Pinson W. H. (1962) A review of the preparation and calibration of shelf and spike solutions currently in use at M.I.T. in the Geochronology Laboratory. Tenth Ann. Progress Report U.S. Atomic Energy Commission Contract AT(30-1)-1381 91-97.

Sardarov S. S. (1961) Bond energy and retention of radiogenic argon in micas. Geochemistry 1, 33-44.

Shapiro L. and Brannock W. W. (1956) Rapid Analysis of Silicate Rocks. U.S.G.S. Bull. 1036-C.

Steyn J. G. D. (1954) Spectrographic and x-ray data on some fluorites from the Transvaal, South Africa. Min. Mag. 30, 327-332.

Tilton G. R., Wetherill G. W., Davis G. L. and Hopson C.A. (1958) Ages of minerals from the Baltimore gneiss near Baltimore, Maryland. Bull. Geol. Soc. Am. 69, 1469-1474.

Wasserberg G. J., Wen T. and Aronson J. (1964) Strontium contamination in mineral analyses. Geochim. et Cosmochim. Acta. 28, 407-410.

Wetherill G. W., Kouvo O., Tilton G. R. and Gast P. W. (1962) Age measurements on rocks from the Finnish precambrian. J. of Geol. 70, 74-88.

APPENDIX A

TREATMENT AND DESCRIPTIONS OF MINERALS

1. Purification of the Minerals

Both biotite samples came from biotite concentrates previously prepared by various workers in the M.I.T. Geochronology Laboratory. These concentrates were first sieved into as many size fractions as possible in the -100, +300 mesh range; where grain size reduction was needed a steel pestle and mortar was used. A size fraction was then spread out on a clean piece of weighing paper and a weak hand magnet was used to remove magnetite. The grains were then passed through a Frantz Isodynamic Magnetic Separator, first at a current of approximately 0.1 amperes and then at a current of approximately 0.36 amperes. Preliminary tests showed that this range of current produced biotites of minimum impurity. The separator had a forward tilt of 25° and a side tilt of 15°. Passages were made at both of these currents until collection was entirely in one cup or the other. This procedure was repeated for every size fraction of interest and the various fractions desired were then collected in one stock bottle for subsequent use in the experiments. All samples of a particular mineral used in the hydrothermal runs came from the one stock bottle.

The pegmatitic albite (cleavlandite) was treated in the same manner as described above for the Ca plagioclase. The main impurity was muscovite and this was effectively removed by magnetic treatment at the maximum current.

The fluorite contained no noticeable impurities. This was a large specimen from a vein mineral deposit. It was reduced to the desired grain size by crushing in a steel mortar and stored in a large stock bottle for subsequent use.

2. Mineral Descriptions

(a) Biotite 3205 is from the Birch Lake Granite, Hart Township, Ontario. Its colour is greenish brown showing some alteration to chlorite. Once again iron oxide and apatite (?) are the main inclusions. Estimate of inclusions is placed at 1% by volume.

(b) Biotite 3138 is from a granitic body 14 miles west of Mount Laurier, Quebec. Its colour is light brown to tan. The main inclusions are zircon with well developed pleochroic haloes, iron oxides and once again a clear mineral, probably apatite. The main inclusion is zircon. Estimate of inclusions is placed at 0.5-1.0%.

(c) The albite is of the cleavlandite variety and is from the Strickland pegmatite, Connecticut. It is part of the whole rock sample R4725 (M.I.T. laboratory collections). The mineral is free of impurities except for some alteration to sericite and kaolinite. The amount varies from grain to grain but is very minor on the whole.

(d) The fluorite is very clean, and no impurities were found. It is a vein fluorite of unknown origin.

APPENDIX B

PREPARATION OF AQUEOUS SOLUTIONS

1. Solution C

1 gram of $CaCO_3$ and 0.5 gram of $KHC_8H_4O_4$ were placed in a weighing bottle and dried overnight at 95°C. They were subsequently removed and placed in a desiccator for 15 minutes, and then weighed. The contents of the weighing bottles were placed in a 1000 ml beaker and dissolved slowly in weak ($\sim$0.1 N) HCL. The beaker was washed repeatedly with distilled demineralized water and the wash added to the volumetric flask. The flask was taken up to volume with distilled demineralized water. The contents were transferred to a 2000 ml polyethylene bottle for storage. After a temperature correction had been made, the solution was found to contain 200.02 μgms Ca/ml and 47.90 μgms K/ml at 20°C.

2. Solutions D and E.

Solution E is a previously prepared potassium standard of $KHC_8H_4O_4$ containing 1030 μgms K/ml. Solution D was prepared by pipetting 2 ml of solution E to a 50 ml volumetric flask, and taking it up to volume with distilled demineralized water. Solution D contains 41.2 μgms K/ml.

PART II

CHAPTER I

INTRODUCTION

The use of the Rb-Sr method for age determinations is based on the decay of Rb^{87} to Sr^{87} by emission of a β^- particle and a neutrino.

Almost from the beginning workers noticed that age determinations on coexisting mineral phases from the same rock specimen gave conflicting ages. Later, when the whole rock method was introduced [Schreiner (1958), Compston and Jeffery (1959), Fairbairn et al (1960) and Allsopp (1961)] it was found that the mineral ages might agree or disagree with the whole rock value. A few examples of this follow.

Tilton et al (1958) found that biotites from the Baltimore Gneiss gave Rb-Sr ages of 300-350 m.y. while the microclines gave results by Rb-Sr that agreed with zircon U-Pb ages of 1100 m.y. Deuser and Herzog (1962) found that biotite-muscovite pairs from pegmatites conflicted in their ages, with biotites always giving the younger age. Wetherill et al (1962) found microcline and muscovite Rb-Sr ages to agree with U-Pb ages at 2700 m.y. but the biotite gave consistent ages of 1800 m.y. Allsopp (1961) compared whole rock and mineral ages. He found that feldspar, biotite and chlorite had lost $*Sr^{87}$, while muscovite, apatite and epidote gained it. He believed that $*Sr^{87}$ migrated by diffusion during a reheating period at 2120 m.y., the age of the biotite sample. Faure et al (1962) found that feldspar both gained and lost $*Sr^{87}$ while the biotite always lost part of its $*Sr^{87}$. Long (1964) took mineral phases from a rock sample which fell on a whole rock isochron giving an age of 530 m.y. with a $(Sr^{87}/Sr^{86})_0$ ratio of 0.710. The mineral phases themselves fell on a separate isochron passing through the whole rock point. This mineral isochron gave an age of 390 m.y. with a $(Sr^{87}/Sr^{86})_0$ ratio of 0.782. He claims that subsequent metamorphism at 390 m.y. was intense enough to cause homogenization of Sr isotopes among minerals in rocks over a wide area.

Generally, Authors believe the loss of $*Sr^{87}$ occurred at a time of intense reheating subsequent to the initial formation of the minerals. McDougall et al (1963) and Gast and Hansen (1962) report that the migration of $*Sr^{87}$ has occurred in rock systems where no visual effects of metamorphism can be found.

These age discrepancies have usually been attributed solely to the addition or loss of $*Sr^{87}$ in the mineral concerned. However Kulp and Engel (1963) and Gerling and Ovchinnkova (1962) have shown that Rb will exchange for K in micas at very low temperatures (room temperature and 100°C). Kulp and Engel were able to lower the Rb/Sr ratio by 25%.

Many other papers have been written dealing with discordant mineral ages and the results obtained are similar to the examples given above. [Craddock et al (1964), Lanphere (1964), Zartmen et al (1964), Fairbairn et al (1964), Fairbairn et al (1963), Lanphere et al (1963), Basset and Giletti (1963), Gerling et al (1962), Wetherill et al (1962), Allsopp et al (1962), Hart (1960), Pinson et al (1958), Aldrich et al (1956).]

To the author's knowledge, the only investigation of Rb and Sr migration under experimental conditions is the work of Deuser (1963). For both muscovite and biotite he found that the order of leachibility was non-radiogenic Sr $>$ $^{*}Sr^{87}$ $>$ Rb and in going from 200°C - 600°C the rate of loss increased greatly. He also noted that non-radiogenic Sr could be easily leached at low temperatures (200°C) but not $^{*}Sr^{87}$. Therefore a marked difference exists between the rate of migration of non-radiogenic Sr and $^{*}Sr^{87}$.

Diffusion studies of an experimental nature concerned with dating methods has been confined primarily to the K-Ar method. However it is believed that some of the results of these investigations should equally well apply to the Rb-Sr method. In general investigators have found that:

(1) Low temperature loss of argon is a desorption process and not volume diffusion [Amirkhonoff et al (1959); Amirkhonoff et al (1959a), Fechtig et al (1960)].

(2) Argon occurs in potassium feldspars and micas in as many as five different positions each with its own activation energy for liberation of the Ar^{40}. They believe the differences in retentivity are due to loose adsorption (low Eact), Ar^{40} located in lattice defects caused by such conditions as perthitization of feldspars (med. Eact) and Ar^{40} locked in a K^{40} site in the crystal lattice (high Eact) [Gerling and Morozova (1957, 1958), Gerling et al (1963), Fechtig et al (1961), Baadsgaard et al (1961), Sardarov (1957) and Hart (1960)].

(3) Some minerals such as sanidine and pyroxene show simple volume diffusion loss with no low temperature "zero" phase of low activation energy [Hart (1960), Fechtig et al (1961), Baadsgaard et al (1961)].

(4) Sardarov (1961) does not believe argon diffuses out of muscovite, but is liberated only when the structural water is given off at high temperature ($> 700^{\circ}$C).

Many other articles have been written concerning the subject of argon loss from minerals, dealing both with the theory of diffusion and the interpretation of the results /Levskii (1963), Amirkhonoff (1961), Everenden et al (1960), Brandt (1962), Gerling (1960) Amirkhonoff et al (1960), Reynolds (1957), Gentner et al (1954), Gentner and Kley (1957)/. In general values of D/a^2 found for minerals fall in the range of 10^{-6} sec^{-1} at temperatures in the range of 1000°C to 10^{-30} sec^{-1} at room temperature, assuming volume diffusion. However, if low temperature loss is by desorption the values at room temperature could be as high as 10^{-18} sec^{-1} /Fechtig et al (op. cit. 1961)/. On the basis of field evidence Hurley et al (1960) set an upper limit for both Ar and Sr diffusion at $\sim 10^{-20}$ sec^{-1} at room temperature.

In a recent paper, Sippel (1963) discusses the self diffusion of sodium in natural minerals. In brief he found that Na diffused from microcline most easily followed by albite-orthoclase-biotite-hornblende and acmite respectively. For albite he got D values of 2.8×10^{-10} cm^2/sec (940°C) and 8×10^{-11} cm^2/sec (850°C). For acmite he got 10^{-11} cm^2/sec (940°C). These values might be some indication of the values to be expected for Sr^{87} diffusion from minerals.

The purpose of this investigation is to study the redistribution of non-radiogenic and radiogenic Sr under controlled conditions of temperature and pressure. Deuser (1963, op. cit.) dealt with single mineral phase and a liquid phase. This investigation carries his work one step farther. Here two mineral phases are placed in contact in the presence of a liquid phase. In this way the movement of Sr from one phase to the other can be studied. From this it may be possible to determine:

(1) the D/a^2 values for both non-radiogenic Sr and $*Sr^{87}$ for the "doner" phase (biotite in this investigation) and the "acceptor" phase (albite or fluorite).

(2) A temperature dependence of the D/a^2 values for biotite.

(3) An equilibrium distribution coefficient for both non-radiogenic Sr and $*Sr^{87}$ and the temperature dependence of this distribution coefficient.

CHAPTER II

EXPERIMENTAL PROCEDURE.

1. Hydrothermal Apparatus.

A. Description of Apparatus

The experiments were performed in a stellite cold seal pressure vessel of the Tuttle type. This bomb is 13.00" in length, 1.250" in outer diameter (OD) and 0.400" in inner diameter (ID). It was connected to the pressure gauge and mechanical pump by means of capillary pressure tubing. The bomb and gauge were isolated from the pump by a needle valve, which also served as a means of releasing pressure if it exceeded the desired value.

The bomb was inserted into an electrically wound furnace, heated by a regulated voltage supply. Temperature recordings at two hour intervals over a two day period showed a maximum variation of $\pm 10^{\circ}C$ once the plateau temperature was reached.

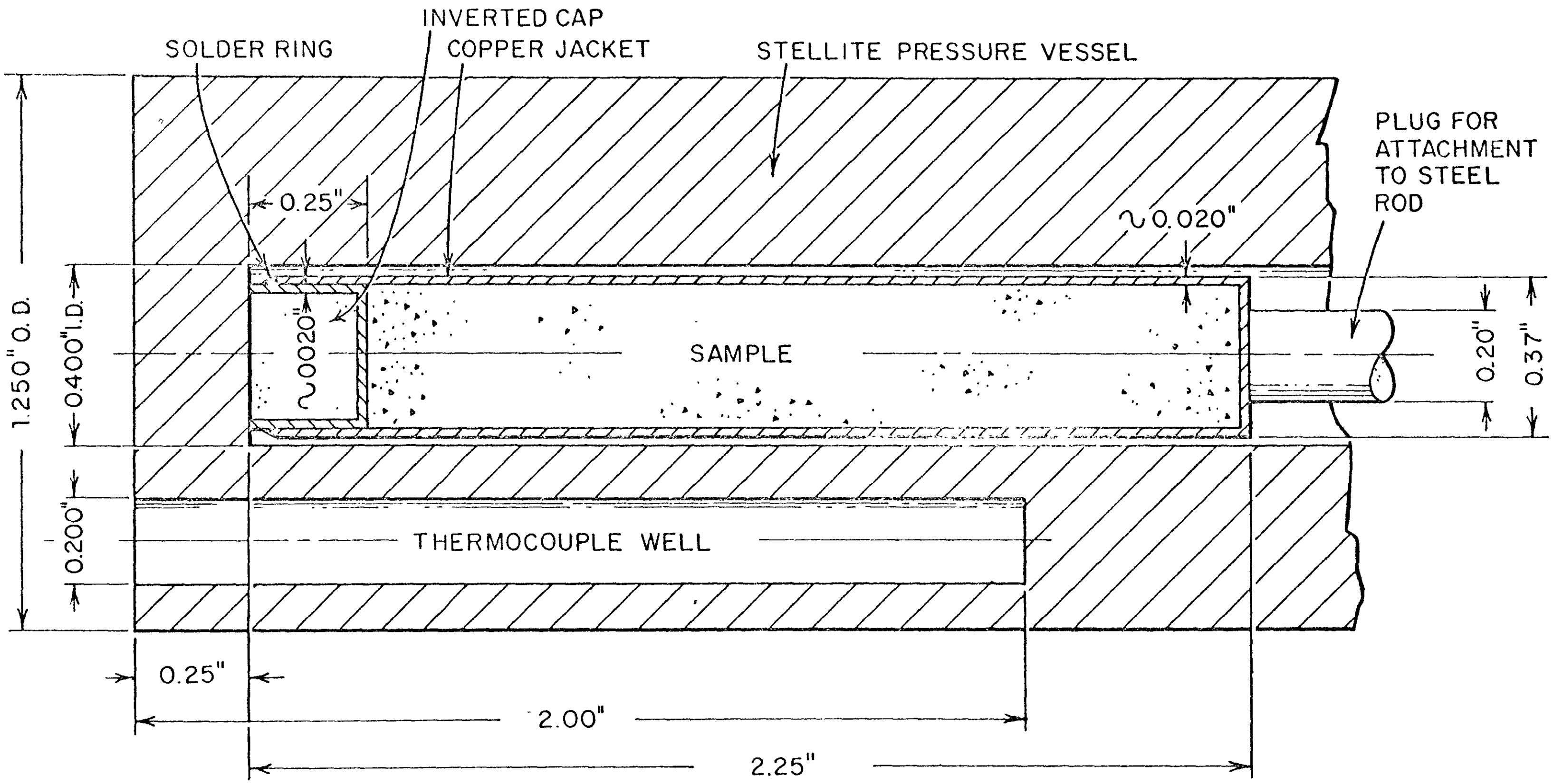
Temperatures were measured with chromel-alumel thermocouples. Before each reading the millivolt potentiometer was calibrated against its standard cell. A new thermocouple was used for each run. It was not passed through an ice bath before connection to the potentiometer, so a room temperature correction was applied to each reading.

Figure 2-1A shows the positioning of the thermocouple in reference to the sample. Measurements showed that approximately a 20°C radial thermal gradient existed between the thermocouple and the sample, while 25-30°C axial gradient existed over the length of the sample region. As the temperature intervals of the runs were 150°C it was believed that the axial gradient could be tolerated.

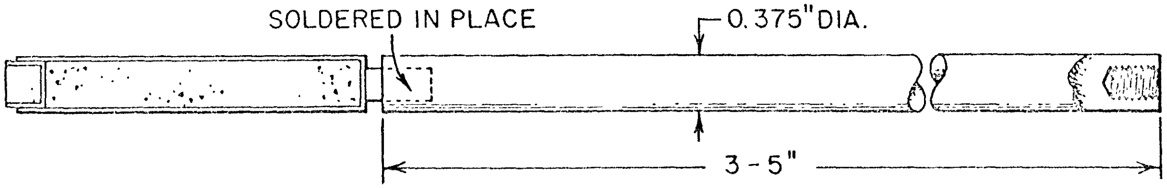
B. Jacket Assembly.

In Figure 2-1 are drawings of the jacket assembly. A of Figure 2-1 shows an enlarged version of the jacket in place in the bomb, and B the jacket assembly drawn to actual size.

These capsules were fabricated from $\frac{1}{2}$" oxygen free copper rod. A small extension was left at the base of the jacket for soldering to a stainless steel rod. This steel rod had two purposes. First, it served as a means by which the assembly was freed from the bomb at the completion of a run. Due to the external pressure exerted on the copper jacket it deformed and could not be dislodged by shaking or tapping. Consequently a long bolt was screwed into a tapped hole at the top of the rod, and by use of a nut, the entire assembly was backed straight out of the bomb. The rod also served as a filler, cutting down greatly on the volume of water needed to build up the desired pressure.



(A) COPPER JACKET IN BOMB (3X ENLARGEMENT)



(B) COPPER JACKET AND STEEL ROD (TRUE SIZE)

FIGURE 2-1 – COPPER JACKET ASSEMBLY.

Pressed into place at the top of the jacket was a tightly fitting inverted copper cap. A ring of solder was formed at the junction of this cap and the jacket wall. It was found necessary to make a narrow, shallow, axial slit on the side of the cap, so that air could escape from the jacket during the heating stage necessary for soldering. If this was not done, the cap invariably popped off, causing a partial loss of the sample. Details of the soldering process will be presented in the next section.

C. Operating Procedure

After fabrication of the jacket, it was soldered to the stainless steel rod. For runs at 450°C or less, it was possible to use "Easy-Flow" silver solder which melted at 1125°F and flowed at 1145°F. Runs carried out at 600°C-750°C needed a high temperature silver solder which both melted and flowed at 1453°F. The jacket and cap were then thoroughly washed with soap and water, rinsed several times with vycor distilled 2N HCL and demineralized H_2O, and dried with acetone. The minerals to be used, which had been previously purified and stored (next section), were quantitatively weighed out using a chain or metlar balance, transferred to a separate piece of weighing paper, thoroughly mixed by coning and added to the jacket. If the solution used was quantitative in nature, it was pipetted in with a calibrated pipette. If only an approximate amount of demineralized water was needed, it was added drop by drop from a plastic squeeze bottle. The same bottle was always used, so that a rough reproducibility was maintained.

Immediately following this addition of solution, the cap was pressed firmly into place using a machine press. The jacket, cap and rod assembly was then immersed in a large bath of cold water until only the top $\frac{1}{2}$" of the jacket extended above the water level (i.e. only that portion containing the cap). This was necessary to keep the mineral and solution cool while heat was applied to the cap. Early attempts to use liquid N_2 failed, because the rapid evaporation rate exposed too much of the jacket to the heat from the torch. Flux was added to the cap, heat applied from a torch using an oxygen-air mixture, and if the components were properly cleaned, the solder flowed quickly and smoothly to form a solid ring connecting the jacket to the cap. The jacket was then cleaned in the lathe of any excess solder and the top trimmed down a few thousands of an inch. The ring of solder was then examined under high power in a microscope to detect any flaws. If any were noted, the soldering process was repeated until a successful job was done. An experiment was performed to see if this soldering process caused any major reaction to occur. The system biotite-albite was used. Table 2-1 lists the results of this run.

Table 2-1 - Experiment 19.

Effect of Soldering on Sample.

	Biotite B3138	Albite R4725	Biotite B3138 #19	Albite R4725 #19
Total Sr:	26.5 ppm.	3.9 ppm.	24.4 ppm.	4.1 ppm.

The jacket was opened immediately after soldering and the minerals separated and analyzed. Assigning a conservative 3% error to these values, it can be seen that very little reaction occurred. Microscopic examination of both minerals showed no change from the untreated minerals.

After emplacement of the pressure vessel in the furnace, an initial 1000-2000 psi water pressure was applied with the hand pump. The valve was then closed and the variac turned up to maximum voltage signalling the beginning of the run. To reach a temperature of 600°C required about 3 hours time, and to attain 750°C entailed 5-6 hours. During the initial heating stage, it was necessary to "bleed off" the pressure several times, and this was done by opening the valve slightly, allowing the water to escape slowly. If a final pressure of 15,000 psi was desired, the minimum value allowed in "bleeding off" was 10,000 psi. This prevented any major pressure changes occurring during the initial stage, eliminating the danger of the jacket bursting. With good judgement and the benefit of experience, it was possible to arrive at the pressure aimed for without having to pump more water into the system.

Once the necessary temperature and pressure were reached, the assembly could be left to run, with only several checks a day needed to keep a continual record of the T-P conditions.

Upon completion of the run, the bomb was quickly quenched in a large container of cold water and the jacket freed in the manner described earlier. The jacket was thoroughly washed to prevent major contamination during the release of the charge. The jacket was then clamped into position above a clean plastic funnel containing hard filter paper (Schleichner and Schell Number 576). Opening of the jacket was accomplished by use of a clean tube cutter, breaking the jacket at the base and top. This allowed the liquid to fall directly onto the filter paper, but the minerals usually required the application of demineralized water to force them out. The original liquid and water were collected in a clean nalgene beaker for analysis. The minerals were washed from the filter paper with acetone into a clean porceline dish and dried with the aid of an infra-red lamp. They were then transferred to a clean sheet of weighing paper for a determination of the percentage recovery. Sometimes an analysis was made of the mixed minerals and a portion was removed at this time. Otherwise they were passed through a Frantz Isodynamic Separator and stored in clean vials for analysis. The separated minerals were always checked under the microscope for their purity. Table 2-2 shows a typical weighing for an experiment. On the average, approximately 98-95% of the original material is recovered. Inspection of steps number (6) and (10) will show that the majority is lost on separation in the magnetic separator. Theoretically, if a homogeneous reaction had occurred, and Sr was evenly distributed throughout the sample, this loss would be of no consequence. However, as discussion will point out, this loss during separation may bear on the discrepancies found.

Table 2-2

Weighing Procedure for Bomb Runs.

A. Before Run

(1) Weight of biotite = 1.9003 grams.

(2) Weight of albite = 0.8510 grams.

(3) Mixed minerals should weigh = 2.7513 grams.

(4) Mixed minerals do weigh = 2.7515 grams.

B. After Run

(5) Weight of mixed minerals = 2.7160 grams.

(6) Recovery of mixed minerals = $\frac{2.7160}{2.7513}$ x100 = 98.7%

(7) Removed for "whole rock" analysis = 0.1513 grams.

(8) Weight of biotite recovered = 1.7118 grams.

(9) Weight of albite recovered = 0.7893 grams.

(10) Total Recovery =

$$0.1513 + 1.7118 + 0.7893 = 2.6524 \text{ grams.}$$

$$= \frac{2.6524}{2.7515} \times 100 = 96.4\%$$

2. Chemistry

A. Isotope Dilution Analysis.

The mineral sample which had been previously cleaned on the Franz magnetic separator, was spread on a clean piece of paper and a representative sample selected by coning and quartering. After weighing, it was transferred to a platinium dish and the Sr spike was added with a calibrated pipette. The dish was placed in a steam bath under a chemical fume hood. For 0.5 grams of sample, 10 ml of distilled reagent grade HF (Shields 1964) and 1.5 ml of 70 per cent vycor distilled $HCLO_4$ was added. Evaporation was completed to near dryness and another portion of HF and $HCLO_4$ were added, and the sample was evaporated again. 150-200 ml of vycor distilled 2N HCL was added, evaporated to approximately 20 ml removed from steam bath and allowed to cool for several hours. The solution was taken up to approximately 40-50 ml with distilled-demineralized water and filtered into a nalgene beaker using hard filter paper (Schleicher and Schnell Number 576). Sr^{85} tracer, for monitoring the ion exchange column separation, was added so that the total count was three times background. The sample was slowly added to a cation exchange column (Dowex 50W - X8, Cross linked, 200 mesh) which had been previously washed with 1000 ml of 2N HCL, making sure not to disturb the resin on the top of the column. After the sample had soaked into the column, an equal volume of 2N HCL was added, carefully washing down the sides of the column in the process. This was repeated once more to insure complete and uniform entry of the sample into the column. 2N HCL was then added until the Sr passed through the columns. This usually required 400 ml of acid. When the Sr was within one-half inch of the bottom, collection in nalgene beakers began. Usually one beaker before, and one beaker after the passage of Sr was taken to gain complete recovery. The beakers were evaporated to dryness on a hot plate. They were then monitored on a gamma counter and only those beakers showing activity were saved. Usually the first beaker to contain a small activity was discarded, thus helping to separate the Ca from the Sr. The Sr was then dissolved in a few mls of 2N HCL, collected into one beaker and again evaporated to dryness. The Sr was taken up in 2-3 ml of 2N HCL, transferred to a 5ml vycor beaker and 2-3 drops of $HCLO_4$ were added to dissolve any resin in the sample. The beaker was evaporated to dryness, and then taken to red heat in a bunsen burner flame to drive off the $HCLO_4$. Approximately 3-4 ml of vycor distilled 6N HNO_3 was added and evaporated to dryness, another portion of acid added and evaporated to dryness again. The beaker was then stored for mass spectrometer analysis.

Early in this investigation pyrex glass beakers and columns were used. However, Wasserberg et al (1964) demonstrated the possibility of Sr exchange between sample and glass to a remarkable extent, and which would not show up in a blank analysis. Therefore, all pyrex glassware was discarded and only vycor glass columns and polyethelene and vycor beakers were subsequently used.

B. Isotope Ratio Analysis.

The procedure is exactly the same as that described above with two exceptions: (1) only an approximate weighing of the sample was done and (2) no Sr spike was added.

C. Sr Spikes.

During the course of this investigation, two Sr spikes were used. The first of these was a Sr^{86} spike, the details of which are presented by Pinson (1962). The average of four isotope ratio analyses are given in Table 2-3.

Table 2-3

Average of 4 Isotope Ratio Analyses of Sr^{86} Spike.

84 = 0.05%
86 = 83.73%
87 = 9.48%
88 = 6.74%

Seven isotope dilution analyses were made using the same M.I.T. shelf solution which contained 7.42 μgms. Sr/ml. Table 2-4 gives the results of the analyses.

The second Sr spike was enriched in both Sr^{84} and Sr^{86}. With a spike of single enrichment, it is not possible to correct for isotopic fractionation, but with the double spike this can be done. Also, once isotopic fractionation is corrected for, the Sr^{87}/Sr^{86} ratio of the sample itself can be determined. An excellent discussion of this double spiking procedure can be found in Krogh (1964). Table 2-5 lists the isotopic ratio and concentration of the spike.

Table 2-4

Isotope Dilution Analysis of Dilute Sr^{86} Spike.

Mass.Spec. Rec. No.	Date	Lab. Rec. Bk. No.	Conc. (μgs Sr/ml)	Analysist
2935(I)	12/13/62	#10,pg.39	2.176	WHP, CCS
2939(I)	12/16/62	#10,pg.39	2.182	WHP, CCS
2940(I)	12/18/62	#10,pg.39	2.179	WHP, CCS
3189(S)	6/13/63	#11,pg.36	2.168	WHP, RMS
3215(S)	6/25/63	#11,pg.36	2.174	WHP, RMS
3379(S)	11/8/63	#11,pg.56	2.173	RHM, TEK
3383(L)	11/12/63	#11,pg.56	2.199	RHM, TEK

Av. = 2.179 μgms. Sr/ml.

(I) = Mass spectrometer Iris
(S) = " " Sally
(L) = " " Lulu
WHP = William H. Pinson
CCS = Charles C. Schnetzler
RMS = Robert M. Shields
RHM = Robert H. McNutt
TEK = Thomas E. Krogh.

Table 2-5

Isotope Ratio and Isotope Dilution Analyses of the Dilute Sr^{84} - Sr^{86} Spike.

Mass Spectrometer

Record Number	Date	Sr^{86}/Sr^{88} Measured	Sr^{86}/Sr^{88} Corrected for Fractionation	Sr^{84}/Sr^{88} Measured	Sr^{84}/Sr^{88} Corrected for Fractionation	Concentration
3414(S)	12.9.63	0.3748	0.3760	0.1418	0.1427	1.051
3415(L)	12.9.63	0.3769	0.3756	0.1435	0.1427	1.050

Av. = 1.050 gms. Sr/ml.

		84 atom %	86 atom %	87 atom %	88 atom %
3424(S)	12.13.63	25.53	50.36	6.95	17.16
3427(L)	12.14.63	25.78	50.41	6.91	16.90
3488(S)	1.10.64	25.68	50.33	6.92	17.06
	Av. =	25.66	50.37	6.93	17.04

Fractionation Corrections (Krogh, 1964) give the final isotopic compositions:

84 = 0.2571 atom fraction
86 = 0.5036 " "
87 = 0.0691 " "
88 = 0.1702 " "

D. Blank Sr.

Contamination level of the analytical procedure is determined by subjecting a known amount of spike Sr to the same chemistry as the Sample. Table 2-6 lists the results of two blank analyses done during the course of this investigation.

Table 2-6

Blank Sr Analyses.

Record Number	Date	Sr^{86}/Sr^{88} ratio Spike	Sr^{84}/Sr^{88} ratio Spike	Sr^{86}/Sr^{88} blank	Sr^{84}/Sr^{88} blank	μgms. Sr/gram.
3528(S)	2.20.64	2.956	1.506	2.190	1.489	0.04
3767(L)	6.3.64	2.956	1.506	2.939	1.497	0.02

The level found is such as to be negligible, as the majority of the runs were in the neighbourhood of 20 μgms Sr/gram Sample.

3. Mass Spectrometry

All runs were done on 6", 60° solid source, single collector mass spectrometers of the Nier type. Magnetic sweeps were used and vibrating reed electrometers amplified the ion currents. Tantalum ribbon, 0.020" x 0.001", was the filament material spot welded to the posts in the source.

A pressure of 2×10^{-7} mm Hg or less was required for isotope ratio and Sr^{84}-Sr^{86} 1D-1R runs for resolution between the 87 and 88 mass peaks. A pressure of 5×10^{-6} mm Hg or less was sufficient for isotope dilution analyses.

Each new filament was cleaned of impurities and checked before use. Up to five Sr analyses per filament were obtained. Between each run, the filament was cleaned to a temperature sufficiently higher than needed for a Sr run. After a Rb analysis, the filament was discarded and the posts and all plates washed with vycor distilled $6NHNO_3$, demineralized H_2O and dried with acetone.

Sr runs required several hours of conditioning at the threshold of emission, limiting production to two runs in a twenty four hour period.

At the beginning of a run, the baseline of the most sensitive scale used was zeroed. Baseline checks were frequent due to machine drift, and the necessary corrections to the peak reading made. As scale changes were necessary, periodic checks on the baseline deflections were needed. A set of 54 sweeps over the desired mass range was sufficient for isotope ratio analyses and 36-54 for isotope dilution. The peaks were recorded on a potentiometric strip chart recorder.

4. Discussion of Errors.

In any discussion of errors a distinction must be made between precision (or reproducibility) and absolute accuracy. Precision is the sum of random errors arising from many sources. Absolute accuracy is an algebraic sum of all systematic errors affecting a measurement. In the complex procedure from hydrothermal apparatus to mass spectrometric analysis, many sources of error are possible and hard to evaluate.

A. Possible Sources of Error.

Possible sources of error in the operating procedure of the hydrothermal apparatus are:

(1) Variation in bomb position in the furnace. This is checked as much as possible by having a collar support at the top of the furnace, and having the bomb stand on lava maintained at a constant level.

(2) Location of the thermocouple in its well. At the beginning of each run the thermocouple was inserted as far as possible into the well, but some subsequent disturbance could alter its position.

(3) Temperature recordings and the stability of the millivolt potentiometer.

(4) Pressure readings and the stability of the gauge.

(5) Reliability of the voltage regulator.

(1) and (2) are random errors varying from run to run and thus affect the precision. (3), (4) and (5) can be considered systematic errors affecting all runs in the same manner.

In chemistry and mass spectrometry the source of error are:

(1) Sample weighing and its contamination with either "normal" or "spike" Sr during chemistry and/or mass spectrometric analysis.

(2) Variation in the instrumental fractionation of the isotopes.

(3) Variation in the rate of emission.

(4) Systematic errors in the VRE scale change, linearity of recorder, or reading of peak heights and baseline.

(5) Lack of resolution due to poor vacuum and/or poor alignment of the filament and sample with the accelerating plate.

(6) Random instabilities or drift in the electronic components.

(7) Random components of the peak height reading error.

(1), (2), (3), (6) and (7) are variables which will affect reproducibility. (4) and (5) will cause a systematic error in a single instrumental set up, or vacuum condition.

B. Reproducibility

(1) Isotope Dilution Analysis

Duplicate analysis of Sr on three mineral samples are given in Table 2-7. They were spiked with the Sr^{84}-Sr^{86} spike and corrected for machine fractionation (Krogh 1964).

Table 2-7

Summary of Duplicate Sr. Analyses

Mineral	Sr ppm	Average	$\bar{\sigma}$	$\bar{E}$	σ	E
Biotite 3205	30.34 29.90	30.12	±0.22	±0.73%	±0.31	±1.03%
Biotite 3138	21.16 21.42	21.29	±0.13	±0.61%	±0.18	±0.84%
Albite R4724	3.78 3.70	3.74	±0.04	±1.07%	±0.06	±1.60%

$$\sigma = \sqrt[2]{\frac{\Sigma d^2}{n-1}}, \qquad \bar{\sigma} = \sqrt[2]{\frac{\Sigma d^2}{n(n-1)}}, \qquad E = \frac{\sigma}{M} \times 100$$

Most of the analyses were done only once. For this purpose σ is a better criteron of the reproducibility. Therefore for Sr analysis > 10 ppm, the precision is ±1%; for Sr < 10 ppm it is ±2%.

Table 7 describes the precision error to be expected on a single analysis in the mass spectrometer.

However, the procedure in this study included the hydrothermal apparatus. One experiment was repeated in its entirety and the results are listed in Table 2-8. The run was performed at a temperature of 600°C, a pressure of 15,000 psi for a time of 45 hours.

Table 2-8

Summary of Sr Data for a Single Experiment done in Duplicate

Mineral	Sr ppm	Average	$\bar{\sigma}$	$\bar{E}$	σ	E
Biotite 3138	10.94 11.21	11.08	±0.13	±1.17%	±0.18	±1.61%
Albite R4725	19.71 21.25	20.48	±0.77	±3.74%	±1.09	±5.38%

$$\sigma = \sqrt[2]{\frac{\Sigma d^2}{n-1}} \qquad \bar{\sigma} = \sqrt[2]{\frac{\Sigma d^2}{n(n-1)}} \qquad E = \frac{\sigma}{M} \times 100$$

For the purpose of this study, an overall precision error (σ) of ± 5% has been assigned to any complete hydrothermal experiment involving isotope dilution analysis.

(2) Isotope Ratio Analysis.

Reproducibility of an isotope ratio analysis can best be seen by listing the results on a standard, run periodically over the course of time by various investigators in the geochronology laboratory at M.I.T. The standard was a $SrCO_3$ (Eimer and Amend, lot number 492327) and the results are listed in Table 2-9.

Table 2-9.

Summary of Data on $SrCO_3$ Standard

(Eimer and Amend Lot Number 492327).

Date	Record Number	Sr^{86}/Sr^{88}	Sr^{87}/Sr^{86}	Sr^{87}/Sr^{86} Corr.	Analyst
12.28.63	3443(s)	0.1179	0.7119	0.7074	EB
1.20.64	3468(S)	0.1182	0.7108	0.7073	TEK
2.28.64	3549(S)	0.1186	0.7098	0.7074	TEK
5.26.64	3743(S)	0.1196	0.7070	0.7075	RMS
6.4.64	3772(S)	0.1199	0.7061	0.7075	RMS
6.28.64	3808(S)	0.1183	0.7112	0.7078	GDR
	Average	0.1187_5	0.7095	0.7075	
	σ =	$\pm$ 0.0008	$\pm$0.0024	$\pm$0.0002	
	E =	$\pm$ 0.67%	$\pm$0.34%	$\pm$0.02%	
	$\bar{\sigma}$ =	$\pm$ 0.0003	$\pm$0.0010	$\pm$0.00007	
	$\bar{E}$ =	$\pm$ 0.28%	$\pm$0.14%	$\pm$0.01%	

$$\sigma = \sqrt[2]{\frac{d^2}{n-1}}, \qquad \bar{\sigma} = \sqrt[2]{\frac{d^2}{n(n-1)}}, \qquad E = \frac{\sigma}{M} \times 100$$

EB = Erna Beiser

TEK = Thomas E. Krogh

RMS = Robert M. Shields

GDR = Glen D. Roe.

Isotope fractionation corrections were applied to all measured Sr^{87}/Sr^{86} ratios assuming the Sr^{86}/Sr^{88} ratio to equal 0.1194 (Nier 1938). This was done as in the following example:

$$\text{Measured } Sr^{87}/Sr^{86} = 0.7092$$

$$\text{Measured } Sr^{86}/Sr^{88} = 0.1191$$

$$\text{Calculated } (Sr^{87}/Sr^{86}) \text{ Corr} = \frac{0.7092}{\frac{0.1194}{0.11925}} = 0.7083$$

i.e. one half the fractionation found for the Sr^{86}/Sr^{88} ratio was applied to the Sr^{87}/Sr^{86} ratio. From Table 9, it can be seen that the fractionation in the Sr^{86}/Sr^{88} ratio is twice that in the uncorrected Sr^{87}/Sr^{86}.

From the data in Table 9 a single isotope ratio analysis is assigned a precision error of ±0.02% for a corrected Sr^{87}/Sr^{86} ratio, and ±0.3% for an uncorrected ratio.

No duplicate isotope ratio measurements are available for the complete procedure, but in the light of results found for isotope dilution analysis, it must be greater than that presented above. For the purposes of this study an arbitrary precision error (σ) of ±1% will be applied.

C. Absolute Accuracy

The best way to estimate accuracy of isotope ratios is to correlate the results in this laboratory with other locations doing the same type of investigation.

An interlaboratory comparison of the Sr^{87}/Sr^{86} ratio of the $SrCO_3$ standard is given in the 11th Annual Report of the M.I.T. Laboratory (1963) and in Faure (1961). The agreement is quite good and gives confidence to the Sr^{87}/Sr^{86} ratios measured. It is recognized however, that the finally established value of the natural Sr^{86}/Sr^{88} ratio may be other than 0.1194, and that all values for Sr^{87}/Sr^{86} normalized to this ratio will have to be modified.

D. Conclusion

Unless otherwise stated, the σ, or reproducibility of a single isotope dilution analysis in this study will be $\pm 5\%$. For a single isotope ratio measurement it will be $+1\%$.

5. Isotope Dilution Calculations

In any isotope dilution analysis, each isotope is a mixture of both normal and spike Sr, so that:

$$\left(Sr^{86} / Sr^{88} \right)_{ID} = \frac{XN + YS}{AN + BS}$$

where N = normal Sr

S = Spike S

ID = isotope dilution

X,Y,A,B = constants denoting the atomic fraction of the isotope in question.

To use the equation, the isotopic composition of both normal and spike Sr must be known. Consider two samples the first with an (Sr^{87}/Sr^{86}) Corr = 1.000 and the second with an (Sr^{87}/Sr^{86})Corr = 0.710.

For the First:

$Sr^{84}/Sr^{86} = 0.0567 = 0.54\% Sr^{84}$

$Sr^{86}/Sr^{86} = 1.0000 = 9.59\% Sr^{86}$

$Sr^{87}/Sr^{86} = 1.0000 = 9.59\% Sr^{87}$

$Sr^{88}/Sr^{86} = \frac{8.3752}{10.4319}(1/.1194) = 80.28\% Sr^{88}$

For the Second:

$Sr^{84}/Sr^{86} = 0.0567 = 0.56\% Sr^{84}$

$Sr^{86}/Sr^{86} = 1.000 = 9.86\% Sr^{86}$

$Sr^{87}/Sr^{86} = 0.7100 = 7.00\% Sr^{87}$

$Sr^{88}/Sr^{86} = \frac{8.3752}{10.1419} = 82.58\% Sr^{88}$

$$\left(^{86}/_{88}\right)_{ID} = \frac{0.0959N + 0.5036S}{0.8028N + 0.1702S} \qquad \left(^{86}/_{88}\right)_{ID} = \frac{0.0986N + 0.5036S}{0.8258N + 0.1702S}$$

The spike values are those of the Sr^{84} - Sr^{86} spike described earlier.

From the equation, a $^{N}/S$ ratio is calculated. However, this is an atomic ratio, and it must be multiplied by weight factor to convert it to a weight ratio. This is done in the following way:

(1) Isotopic Composition of Sr^{84}-Sr^{86}

spike = 0.2566 Sr^{84}

0.5036 Sr^{86}

0.0691 Sr^{87}

0.1702 Sr^{88}

(2) Atomic weight = 0.2566 x 84 = 21.5544

0.5036 x 86 = 43.3096

0.0691 x 87 = 6.0117

0.1702 x 88 = 14.9776

85.8533

(3) Isotopic Composition of Example 1 = 0.0567 Sr^{84}

0.0959 Sr^{86}

0.0959 Sr^{87}

0.8028 Sr^{88}

(4) Atomic Weight = 0.0567 x 84 = 0.4763

0.0959 x 86 = 8.2474

0.0959 x 87 = 8.3433

0.8028 x 88 = 70.6464

87.7134

(5) Weight Factor = $\frac{87.7134}{85.8533}$ = 1.022

(6) $(^{N}/_{S})_{wt} = (^{N}/_{S})_{atomic} \times 1.022$

(7) $N(ppm) = \frac{R \times S}{W}$ where $R = (^{N}/_{S})_{wt}$

S = concentration of spike in μgms.

W = weight of sample in grams.

The above discussion would apply to a spike of single enrichment. In the case of the Sr^{84}-Sr^{86} double spike, a $(Sr^{84}/Sr^{88})_{ID}$ ratio is also used, and a $(N/S)_{wt}$ ratio is calculated in exactly the same manner as above. If no fractionation has occurred, both $(^{N}/_{S})_{wt}$ values should be the same. However, this is rarely the case. It therefore becomes necessary to apply a fractionation correction to both the $(Sr^{86}/Sr^{88})_{ID}$ and $(Sr^{84}/Sr^{88})_{ID}$ so that a common $(^{N}/_{S})_{wt}$ ratio does result (Krogh 1964). As in the case of fractionation corrections to the Sr^{87}/Sr^{86} ratio, these isotope dilution fractionation corrections do improve the reproducibility.

CHAPTER III

ANALYTICAL RESULTS.

1. Introduction

Tables 1 through 18 list the analytical results obtained on the successful hydrothermal runs. The tables have been broken up in the following way:

Part (1) gives the mineral and aqueous phases involved and the quantity of each used. Tables 1 to 5 also give in part (1) the concentration and isotopic composition of the Sr for each phase.

Part (2) lists the temperature in degrees centigrade (°C), the pressure in pounds per square inch (psi) and the time in hours under which the particular experiment was run.

Part (3) lists the results of the mass spectrometric analyses. The data for the minerals at the beginning of each run are also listed, so that a direct comparison can be made on the magnitude of Sr movement.

Part (4) converts the data from part (3) to micrograms (μgms) for each Sr isotope involved. The column headed "loss" shows the magnitude of the discrepancy found between analysis before the run and analysis after the run. This problem will be discussed in the next chapter. All numbers are calculated on the assumption that non-radiogenic strontium (designated Sr^n) has

An Sr^{84}/Sr^{88} ratio = 0.0068, a Sr^{86}/Sr^{88} ratio = 0.1194 and a (Sr^{87}/Sr^{86}) = 0.710. The numbers in part (4) are calculated on the assumption that the results in part (3) are representative of the entire mineral phase originally put into the bomb, not just the fraction finally recovered.

The symbol $(Sr^{87}/Sr^{86})_0$ will be used throughout this report to designate the Sr^{87}/Sr^{86} ratio of the non-radiogenic Sr (Sr^n) as opposed to the measured or calculated ratio which include the $*Sr^{87}$ component.

Unless otherwise stated, all biotite and liquid Sr^{87}/Sr^{86} ratios from experiment 9 to 24 have been calculated from Sr^{84}-Sr^{86} isotope dilution analyses. All other Sr^{87}/Sr^{86} ratios including the untreated biotites have been measured directly by isotope ratio analyses.

As stated in the previous chapter, the error on a single isotope dilution analysis is ±5% and on a single isotope ratio measurement, ±1%. All figures giving error limits of one standard deviation (σ) are the result of duplicate or triplicate analyses.

The descriptions of the minerals can be found in Appendix A. Appendix B describes the method of preparation of the various aqueous solutions used in the course of this investigation.

Table 3-1. Data on Experiment 2.

(1) Components: 1.009 grams Calcium plagioclase having 824 ppm Sr with a Sr^{87}/Sr^{86} ratio = 0.705 Mesh size -100, +200.

Solution A:

1.000 ml aqueous solution having 20.67 μgms Sr/ml with the isotopic composition:

53.48% Sr^{84}
14.03% Sr^{86}
4.23% Sr^{87}
28.26% Sr^{88}

(2) Conditions: 600°C, 15,000 psi, 113 hours.

(3) Results

Before		After	
Plagioclase	Solution	Plagioclase	Solution*
$\frac{Sr^{84}}{Sr^{86}} = 0.0568$	20.67 μgms.	$\frac{Sr^{84}}{Sr^{86}} = 0.1849$	(1)0.23 μgms. (2)0.70 μgms.

*(1) Calculated for normal Sr with Sr^{87}/Sr^{86} = 0.710.

(2) " " pure Sr^{84} spike solution with isotopic composition given above.

EXPERIMENT 2.

Discussion

This experiment was performed to test the idea that Sr is easily assimilated by the feldspar lattice. As Sr in the feldspar is low in Sr^{84} and the spike is enriched in this isotope the Sr^{84}/Sr^{86} ratio is the most sensitive indicator of any movement of Sr from the liquid to the mineral.

If 20.67 μgms of Sr from the solution were added to the 824 gms of Sr in the mineral, the Sr^{84}/Sr^{86} ratio that would result can be calculated as follows:

$$
\begin{aligned}
Sr^{86} \text{ in plagioclase} &= Sr^{86} \text{ originally in plagioclase} \\
&\quad + Sr^{86} \text{ from liquid phase} \\
&= 824 \text{ ppm X } 1.009 \text{ grams X } 0.0986 \\
&\quad + 20.67\, \mu\text{gms/ml X 1 ml X } 0.1403 \\
&= 81.98\, \mu\text{gms} + 2.90\, \mu\text{gms} = 84.88\, \mu\text{gms.} \\
Sr^{84} \text{ in plagioclase} &= Sr^{84} \text{ originally in plagioclase} \\
&\quad + Sr^{84} \text{ from liquid phase} \\
&= 824 \text{ ppm X } 1.009 \text{ grams X } 0.0056 \\
&\quad + 20.67\, \mu\text{gms/ml X 1 ml X } 0.5348 \\
&= 4.66\, \mu\text{gms} + 11.07\, \mu\text{gms} = 15.73\, \mu\text{gms.}
\end{aligned}
$$

This would give:

$$Sr^{84}/Sr^{86} = \frac{15.73}{84.88} = 0.1853$$

Conclusion

The above answer agrees very well with the result of mass spectrometric analysis. This suggests that the Sr has moved from the liquid phase to the mineral and it is supported by the results of analysis on the liquid phase. In the latter, the maximum amount of Sr that is found is 0.70 μgms, calculated on the basis that it is pure Sr^{84} spike.

Table 3-2. Data on Experiment 4.

(1) Components: 1.000 grams Calcium plagioclase having 824 ppm Sr with a Sr^{87}/Sr^{86} ratio = 0.705; Mesh size: -100, +200

Solution B:

1.000 ml aqueous solution having 39.19 μgms. Sr/ml with the isotopic composition:

53.48% Sr^{84}
14.03% Sr^{86}
4.23% Sr^{87}
28.26% Sr^{88}

(2) Conditions: 600°C, 15000 psi, 88 hours.

(3) Results.

Before		After	
Plagioclase	Solution	Plagioclase	Solution*
$\frac{Sr^{84}}{Sr^{86}} = 0.0568$	39.19 μgms.	$\frac{Sr^{84}}{Sr^{86}} = 0.2892$	(1)5.50 μgms (2)16.80 μgms

*(1) Calculated assuming normal Sr with $Sr^{87}/Sr^{76} = 0.710$.

(2) " " pure Sr^{84} spike solution with isotopic composition given above.

EXPERIMENT 4

Discussion

This experiment is essentially a repeat of the previous one, only with a more concentrated aqueous phase. As before the Sr^{84}/Sr^{86} ratio that would result if 39.19μgms of Sr^{84} spike were added to the plagioclase is:

$$Sr^{84}/Sr^{86} = \frac{25.57}{86.75} = 0.2948$$

Conclusion

Once again the Sr has left the liquid phase and moved to the mineral as the calculated and analysed answers agree within experimental error. Therefore the results calculated for the liquid phase mean either contamination from some source or that the mineral partially dissolved and liberted some Sr to the aqueous phase. Dissolution is improbable as it was not noted in the previous experiment which was treated as the same T and P for a greater time interval.. Therefore the analysis on the liquid phase probably represent some form of laboratory contamination.

Table 3-3. Data on Experiment 5.

(1) Components: 0.9986 grams of biotite 3086 having 19.60 ppm Sr with a Sr^{87}/Sr^{86} ratio = 10.46; Mesh size: -100, +200

Solution A:

1.000 ml aqueous solution having 20.67 μgms. Sr/ml with the isotopic composition:

53.48% Sr^{84}
14.03% Sr^{86}
4.23% Sr^{87}
28.26% Sr^{88}

(2) Conditions: 600°C, 15000 psi, 111 hours.

(3) Results:

Before		After	
Biotite 3086	Solution	Biotite 3086	Solution*
$\frac{Sr^{84}}{Sr^{86}} = 0.0568$	20.67 μgms.	$\frac{Sr^{84}}{Sr^{86}} = 2.794$	(1) 0.35 μgms (2) 1.1 μgms

*(1) Calculated assuming normal Sr with $Sr^{87}/Sr^{86} = 0.710$.

(2) " " pure Sr^{84} spike solution with isotopic composition given above.

EXPERIMENT 5.

Discussion

Here the mineral phase has been changed to a biotite. It was treated under the same conditions as the plagioclase in the two previous experiments. As before if 20.67μgms of Sr from the liquid was added to 19.60 gms in the biotite the resulting Sr^{84}/Sr^{86} ratio would equal 2.86. Using the trial and error method, it is found that 19.0-19.5μgms of the Sr from the solution would have to be added to the biotite to give the observed Sr^{84}/Sr^{86} ratio.

Conclusion

The Sr from the liquid phase has moved to the biotite leaving the former with a maximum of 1.1μgms of the original Sr.

Table 3-4. Data on Experiment 6.

(1) Components used:

Component	Isotopic Composition	Concentration	Amount used
Calcium plagioclase(-100,+200)	Sr^{87}/Sr^{86} = 0.705	824 ppm	1.0116 grams
Biotite 3086 (-100,+200)	Sr^{87}/Sr^{86} = 10.46	19.60 ppm	1.0082 grams
Aqueous Solution A	53.48% Sr^{84} 14.03% Sr^{86} 4.23% Sr^{87} 28.26% Sr^{88}	20.67 μgms/ml.	1.000 ml.

(2) Conditions: 600°C, 15000 psi, 181 hours.

(3) Results:

	Biotite 3086	Plagioclase	Solution
Isotopic Composition	16.01% Sr^{84} 8.27% Sr^{86} 28.31% Sr^{87} 47.40% Sr^{88}	0.89% Sr^{84} 9.95% Sr^{86} 6.93% Sr^{87} 82.37% Sr^{88}	N.D.*
Isotope Dilution	40.57 ppm	N.D*	(1) 1.50 (Sr^{87}/Sr^{86} = 0.710) (2) 4.95 (Sr^{84} spike)

(4) Sr Migration

	Before			After		
	Biotite 3086	Plagioclase	Solution	Biotite 3086	Plagioclase	Solution
Sr^{84}	0.06 μgms.	4.65 μgms.	11.05 μgms.	6.50 μgms.	N.D.*	N.D.*
Sr^{86}	1.00 "	81.94 "	2.90 "	3.36 "		
Sr^{87}	10.43 "	57.76 "	0.87 "	11.49 "		
Sr^{88}	8.35 "	686.00 "	5.84 "	19.23 "		
Sr^{84}/Sr^{86}	0.0568"	0.0568"	3.812 "	1.936"	0.090	N.D.*

* N.D. = not determined

EXPERIMENT 6

Discussion

Here the two mineral phases used previously have been combined into a single experiment. In this way it is possible to study the partition of Sr among the phases involved.

Isotope dilution analysis on the biotite gives 40.57 ppm which means that 20.97 X 1.0082 = 21 μgms of Sr has been added to this mineral. By using the trial and error method it was found that the addition of 12 μgms of Sr from the aqueous solution and of 9 μgms of Sr of normal composition (from the plagioclase) would result in the following isotopic composition:

16.10% Sr^{84}
8.80% Sr^{86}
28.00% Sr^{87}
47.00% Sr^{88}

This agrees very well with analysed results.

If the remaining 9 μgms of Sr from the liquid were added to the plagioclase the Sr^{84}/Sr^{86} ratio would be 0.114. The analysed value is 0.090 and to achieve this latter requires the addition of 5 μgms of Sr from the liquid. Isotope dilution analysis on the liquid phase itself shows that a maximum of 4.95 μgms of Sr 84 spike could remain in the liquid.

Conclusion

If 12 μgms of Sr^{84} spike goes to the biotite, 5 μgms to the plagioclase and 5 μgms remains in the liquid, a fair balance was achieved and agrees with mass spectrometric analysis. Therefore a qualitative statement can be made to the effect that Sr from the liquid phase has partitioned itself in favour of the biotite.

Table 3-5. Data on Experiment 7.

(1) Components used:

Component	Isotopic Composition	Concentration	Amount used
Calcium plagioclase(-100,+200)	Sr^{87}/Sr^{86}= 0.705	.824 ppm	1.0003 grams
Biotite 3086 (-100,+200)	Sr^{87}/Sr^{86}=10.46	19.60 ppm	0.9998 "
Aqueous Solution A	53.48% Sr^{84} 14.03% Sr^{86} 4.23% Sr^{87} 28.26% Sr^{88}	20.67μgm/ml.	1.000 ml.

(2) Conditions: 600°C, 15000 psi, 36 hours.

(3) Results:

	Biotite 3086	Plagioclase	Solution
Isotopic Composition	7.25% Sr^{84} 8.79% Sr^{86} 21.99% Sr^{87} 61.97% Sr^{88}	0.67% Sr^{84} 9.91% Sr^{86} 6.94% Sr^{87} 82.54% Sr^{88}	N.D.
Isotope Dilution	63.30 ppm	N.D.	N.D.

(4) Sr Migration

	Before			After		
	Biotite 3086	Plagioclase	Solution	Biotite 3086	Plagioclase	Solution
Sr^{84}	0.05μgms.	4.61μgms.	11.05μgms.	4.59μgms.	N.D.	N.D.
Sr^{86}	0.99 "	81.24 "	2.90 "	5.56 "		
Sr^{87}	10.31 "	57.27 "	0.87 "	13.92 "		
Sr^{88}	8.24 "	681.00 "	5.84 "	39.23 "		
Sr^{84}/Sr^{86}	0.0568"	0.0568"	3.812"	0.8248"	0.0676	N.D.

EXPERIMENT 7

Discussion

This is a repeat of experiment 6 with a shorter time interval. The reasons for performing this experiment are the same as described earlier.

As before the trial and error method shows that the addition to the biotite of 10 μgms of Sr^{84} spike and 34 gms of Sr of normal composition gives:

61.5% Sr^{88}
20.5% Sr^{87}
9.1% Sr^{86}
8.8% Sr^{84}

This agrees fairly well with the observed value. Also, adding 2.5 μgms of this spike Sr to the plagioclase will result in the observed Sr^{84}/Sr^{86} ratio in that mineral. This means that approximately 8 μgms must have remained in the liquid phase. This cannot be verified as the liquid was not analysed in this experiment.

Conclusion

Once again it is seen that the biotite takes up more Sr from the liquid phase than the plagioclase. The cause of the apparent movement of normal Sr from the plagioclase to the biotite in both experiment 6 and 7 will be discussed in the next chapter.

Table 3-6 Data on Experiment 9

(1) Components: 1.5054 grams Biotite 3205 (-100, +270)

0.7489 grams fluorite (-100, +230)

~0.5 ml. demineralized H_2O

(2) Conditions: 750°C, 3000 psi, 97 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60± 0.22	4.48± 0.02	2.145	36.45	4.32
Fluorite	0.7095	20.82± 0.04	0	0.790	24.32	0.11
Water	-	-	-	N.D.	1.76 μgms total	N.D.

(4) Sr Migration

	Before			After			
Isotope	Biotite	Fluorite	Total	Biotite	Fluorite	Total	Loss
Sr^{84}	0.26 μgms.	0.09	0.35	0.27 μgms	0.10	0.37	-0.02
Sr^{86}	4.62 "	1.54	6.16	4.77 "	1.79	6.56	-0.40
Sr^{87}	3.27 "	1.09	4.36	3.39 "	1.27	4.66	-0.30
Sr^{88}	38.68 "	12.87	51.55	39.94 "	14.97	54.91	-3.36
$*Sr^{87}$	6.74 "	0	6.74	6.50 "	0.08	6.58	+0.16
Total	53.57 "	15.59	69.16	54.87 "	18.21	73.08	-3.92

EXPERIMENT 9

Discussion

Beginning with this experiment, attempts were made to transfer Sr, both Sr^n and radiogenic Sr^{87} (designated $*Sr^{87}$) from the mineral biotite to an acceptor phase. In this experiment the acceptor phase was chosen to be fluorite. The minor liquid phase of demineralized water was added in the belief that it would act solely as a carrier phase for the transfer of strontium.

This run was performed at a temperature and total pressure (including Po_2) far outside the stability limits of biotites /Eugster (1959)7. Microscopic examination following the run showed a marked development of black opaque material coupled with a slight colour change to a lighter brown. Fractures filled with the opaque material were evident and the biotite showed undulatory extinction under crossed nicols. In general it must be concluded that the biotite has suffered a partial alteration and perhaps shows the beginning stages of recrystallization. The fluorite mineral has gone from a clear mineral to a gray cloudy mineral. Investigation under the highest power in the petrographic microscope could not determine any evidence of biotite inclusions. No noticeable changes in the index of refraction was seen.

Looking at the data it is seen that the biotite has lost a negative amount of Sr^n while the fluorite has gained a positive amount. At first this run was discarded as a failure because of known contamination with tap water due to a leak in the jacket. It is included solely to test the movement of $*Sr^{87}$. It is believed that tap water would not appreciably effect this isotope. Therefore looking at $*Sr^{87}$ only we see that the biotite has lost 3.5% of its Sr^{87} at 750°C in 97 hours, while the fluorite has taken up 1.2%. Since the amount transferred is very small, the discrepancy could be experimental error.

Conclusion

The biotite has given up a maximum of 3.5% of its $*Sr^{87}$ at 750°C in 97 hours. This mineral has suffered considerable alteration during the course of the run.

Table 3-7 Data on Experiment 10.

(1) Components: 1.5250 grams Biotite 3205 (-100, +270)

0.7556 grams Fluorite (-100, +230)

0.5 ml demineralized water.

(2) Conditions: 750°C, 3000 psi, 210 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60± 0.22	4.48± 0.02	2.20	31.72	4.06
Fluorite	0.7095	20.82± 0.04	0	0.913	22.36	0.45

(4) Sr Migration

	Before			After			
Isotope	Biotite	Fluorite	Total	Biotite	Fluorite	Total	Loss
Sr^{84}	0.27 μgms.	0.09	0.36	0.24	0.09	0.33	0.03
Sr^{86}	4.68 "	1.55	6.23	4.17	1.63	5.80	0.43
Sr^{87}	3.32 "	1.10	4.42	2.96	1.16	4.12	0.30
Sr^{88}	39.19 "	12.99	52.18	34.96	13.68	48.64	3.54
$*Sr^{87}$	6.83 "	0	6.83	6.19	0.34	6.53	0.30
Total	54.29 "	15.73	70.02	48.52	16.90	65.42	4.60

EXPERIMENT 10

Discussion

This experiment is the same as number 9 except that it was carried out for a longer time interval. Once again the T-P conditions are far outside the stability limits for biotite. The same alteration effects on the minerals were noted.

In this experiment biotite has lost 5.3μgms of Sr^n, and 0.63μgms of $*Sr^{87}$ while the fluorite has gained 0.82 and 0.34μgms of Sr^n and $*Sr^{87}$ respectively. This is 9.2% loss and 5.0% gain of $*Sr^{87}$ from the biotite and to the fluorite respectively. That is using the biotite data 9.2% of the $*Sr^{87}$ was lost and using the fluorite data, 5.0% was lost. This leaves a met imbalance of 4.60μgms of Sr of which 0.30μgms is $*Sr^{87}$.

Conclusion:

Both Sr^n and $*Sr^{87}$ have been lost from the biotite at 750°C in 210 hours. The maximum loss was 9.2% for $*Sr^{87}$ and 11.0% for Sr^n. Once again the biotite mineral has suffered considerable alteration.

Table 3-8. Data on Experiment 12.

(1) Components: 3.0025 grams Biotite 3205 (-100, +270)

0.7517 grams Fluorite (-100, +230)

Solution C:~0.5 ml Ca^{++} - K^{+} Solution containing

200 μgms Ca/ml and 48 μgms K/ml.

(2) Conditions: 650°C, 8000 psi for 216 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr (ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr (ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60± 0.22	4.48± 0.02	2.153	35.13	4.40
Fluorite	0.7095	20.82± 0.04	0	0.714	22.15	0.01
Ca^{++}-K^{+} Solution	N.D.	0.15 μgm/ml	N.D.	N.D.	N.D.	N.D.

(4) Sr Migration

	Before			After			
Isotope	Biotite	Fluorite	Total	Biotite	Fluorite	Total	Loss
Sr^{84}	0.52 μgms	0.09	0.61	0.52	0.09	0.61	0
Sr^{86}	9.21	1.54	10.75	9.10	1.64	10.74	0
Sr^{87}	6.54	1.10	7.64	6.46	1.16	7.62	0.01
Sr^{88}	77.16	12.92	90.08	76.20	13.74	89.94	0
$*Sr^{87}$	13.45	0	13.45	13.21	0.01	13.22	0.23
Total	106.88	15.65	122.53	105.49	16.64	122.13	0.23

EXPERIMENT 12

Discussion

This experiment increased the ratio of biotite/fluorite from 2/1 to 4/1. The temperature was decreased 100°C and the pressure increased. Also the aqueous phase now contains 200μgms Ca/ml and 48μgms K/ml. This solution was introduced in the belief that it would cause an exchange reaction to occur between Sr in the biotite and the Ca and/or K in the solution. Once the Sr was liberated from the biotite it should then move to the fluorite. As seen from the table no reaction has occurred. The maximum amount of Sr^n and $^*Sr^{87}$ lost from the biotite is 1-2%. This is verified with the fluorite data where the Sr^{87}/Sr^{86} ratio has increased only from 0.710 to 0.714. It appears that the presence of the Ca-K solution had no effect in moving Sr from the biotite.

Conclusion

By decreasing the temperature 100°C the reaction has been effectively stopped. A maximum loss of both $^*Sr^{87}$ and Sr^n is 1-2%.

Table 3-9. Data on Experiment 13.

(1) Component: 1.9986 grams Biotite 3205 (-100, +270)

1.0014 grams Cleavlandite (-100, +200)

Solution C: ~ 0.5 ml Ca^{++}-K^{+} Solution containing 200 μgm/ml Ca and 48 μgm/ml K

(2) Condition: 650°C, 7500 psi, 115 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60 ± 0.22	4.48 ± 0.02	2.64	25.85	4.12
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	1.04	15.97	0.50
Solution	N.D.	N.D.	N.D.	~0.76	1.2 μgms	N.D.

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.35 μgm	0.02	0.37	0.24	0.09	0.33	0.02
Sr^{86}	6.13	0.37	6.50	4.28	1.53	5.81	0.69
Sr^{87}	4.35	0.26	4.62	3.04	1.08	4.12	0.50
Sr^{88}	51.36	3.09	54.45	35.86	12.79	48.65	5.80
$*Sr^{87}$	8.96	0.08	9.03	8.23	0.50	8.73	0.30
Total	71.14	3.82	74.97	51.65	15.99	67.64	7.31

EXPERIMENT 13

Discussion

A new acceptor was introduced with this experiment while the same biotite was kept. The biotite/albite ratio was 2/1 and the Ca-K solution was also retained. The biotite here, as in the last experiment showed considerable alteration. Using the biotite data, this mineral has lost 30% of its Sr^n and 8% of its $*Sr^{87}$. Using the albite data, the biotite has lost 19% of its Sr^n and 4.8% of its $*Sr^{87}$. This liquid phase was found to contain 1.2 μgms of Sr with a Sr^{87}/Sr^{86} ratio = 0.76. However looking at the "lost" column, the Sr^{87}/Sr^{86} ratio of the Sr that was not recovered should be $\sim$ 1.2.

Conclusion

The biotite, showing considerable alteration, has lost a maximum of 30% and 8% of its Sr^n and $*Sr^{87}$ respectively at 650°C in 115 hours, in the presence of the cleavlandite "acceptor" phase.

Table 3-10. Data on Experiment 14.

(1) Components: 1.9993 grams Biotite 3205 (-100,+270)

0.9981 grams Cleavlandite (-100,+200)

Solution C: ~0.5 ml Ca-K solution containing

200 μgms/ml Ca and 48 μgms/ml K

(2) Conditions: 650°C, 7,500 psi, 405 hours.

(3) Results:

	Before				After	
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3205	2.110	35.60± 0.22	4.48± 0.02	2.94	24.03	4.33
Cleavlandite	0.9454	3.82± 0.03	0.08± 0.01	1.08	16.46	0.58

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.35μgm	0.02	0.37	0.22	0.09	0.31	0.04
Sr^{86}	6.13	0.37	6.50	3.88	1.56	5.44	1.06
Sr^{87}	4.36	0.26	4.62	2.76	1.11	3.87	0.75
Sr^{88}	51.38	3.08	54.46	32.52	13.09	45.61	8.85
$*Sr^{87}$	8.96	0.08	9.04	8.66	0.58	9.24	-0.20
Total	71.18	3.81	74.99	48.04	16.43	64.47	10.50

EXPERIMENT 14.

Discussion

This is the same as experiment 13 carried on for a longer time interval, to see if an equilibrium condition could be reached for both Sr^n and $^*Sr^{87}$. The biotite data states that 33% and 3% of the Sr^n and $^*Sr^{87}$ respectively have been lost. The cleavlandite data states that 19.5% and 5.6% of Sr^n and $^*Sr^{87}$ respectively have been lost. Therefore the cleavlandite data shows a progressive loss of $^*Sr^{87}$ with time while the biotite suggests just the opposite. As far as Sr^n is concerned, it appears that its movement has essentially ceased.

Conclusion

A maximum of 33% and 5.6% of Sr^n and $^*Sr^{87}$ have been lost at 650°C in 405 hours.

Table 3.11. Data on Experiment 16.

(1) Components: 1.8993 grams of Biotite 3138 (-100,+120)

0.8479 grams of Cleavlandite (-60, +100)

~0.5 ml. demineralized water

(2) Conditions: 600°C, 15000 psi, 45 hours.

(3) Results.

	Before				After *	
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.16	5.11 ± 0.04	5.37	16.07	5.06
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.824	19.91	0.18

*All values calculated from isotope dilution analyses.

(4)Sr Migration

	Before					After	
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.22 μgms	0.02	0.24	0.12	0.09	0.21	0.03
Sr^{86}	3.99	0.31	4.30	2.06	1.65	3.71	0.59
Sr^{87}	2.83	0.22	3.05	1.46	1.17	2.63	0.42
Sr^{88}	33.39	2.62	36.01	17.27	13.80	31.04	4.97
$*Sr^{87}$	9.71	0.07	9.78	9.61	0.17	9.78	0
Total	50.14	3.24	53.38	30.52	16.88	47.37	6.01

EXPERIMENT 16

Discussion

Beginning with this experiment and following through to the end, the system is composed of the same cleavlandite as used previously but with a new biotite. All the runs except the last two use only demineralized water as the liquid phase. The biotite always shows some degree of alteration but not to the marked extent seen for experiments 9-12.

In experiment 16 the Sr^{87}/Sr^{86} ratio in the biotite has increased greatly while it has decreased in the cleavlandite. The biotite data states that 48.5% and ~1% of the Sr^n and $^*Sr^{87}$ respectively have been lost. The albite data states that 33% and 0.8% Sr^n and $^*Sr^{87}$ respectively have been lost from the biotite. The discrepency that exists between biotite and albite consists almost entirely of Sr^n.

Conclusion

A maximum of 33% and 1% Sr^n and $^*Sr^{87}$ respectively have been lost from the biotite at 600°C in 45 hours.

Table 3-12. Data on Experiment 17.

(1) Components: 1.8984 grams Biotite 3138 (-100, +120)

0.8479 grams Cleavlandite (-60,+100)

~0.5 ml demineralized water

(2) Conditions: 600°C, 15000 psi, 112 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.16	5.11 ± 0.04	6.06	14.85	5.07
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.842	20.00	0.23
Water	-N.D.	-N.D	-N.D.	0.738	~1.1 µgm/ml.	N.D.

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.23 µgms	0.02	0.25	0.10	0.09	0.19	0.06
Sr^{86}	3.98 "	0.31	4.29	1.83	1.65	3.48	0.81
Sr^{87}	2.83 "	0.22	3.05	1.30	1.17	2.47	0.58
Sr^{88}	33.37 "	2.62	35.99	15.34	13.84	29.18	6.81
$*Sr^{87}$	9.70 "	0.07	9.77	9.62	0.20	9.82	-0.05
Total	50.11 "	3.24	53.35	28.19	16.95	45.14	8.21

EXPERIMENT 17

Discussion

This is the same experiment as 16 except for the time interval involved. The biotite data shows that 54% and 1% Sr^n and $^*Sr^{87}$ have been lost, while the albite data states that 33% and 1.2% Sr^n and $^*Sr^{87}$ have been lost from the biotite. The liquid phase was found to contain approximately 1.1 μgms in total with an Sr^{87}/Sr^{86} ratio $\cong 0.74_0$. The Sr loss is again found to be Sr^n.

Conclusion

The biotite has lost a maximum of 54% and 1.2% of Sr^n and $^*Sr^{87}$ respectively. No increase in the concentration of Sr in the albite is noted between experiment 16 and 17.

Table 3-13. Data on Experiment 18.

(1) Components: 1.8974 grams Biotite 3138 (-100, +120)

0.8479 grams Albite (-60, +100)

~ 0.5 ml. demineralized water.

(2) Conditions: 450°C, 7500 psi, 118 hours.

(3) Results:

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$^*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$^*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.16	5.11 ± 0.04	5.17	16.56	5.04
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.779	17.29	0.15

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.23 μgms	0.02	0.25	0.12	0.08	0.20	0.03
Sr^{86}	3.98	0.31	4.29	2.16	1.43	3.54	0.75
Sr^{87}	2.83	0.22	3.05	1.53	1.02	2.55	0.50
Sr^{88}	33.36	2.62	35.98	18.05	12.00	30.05	5.93
$^*Sr^{87}$	9.70	0.07	9.77	9.56	0.13	9.69	0.08
Total	50.10	3.24	53.34	31.42	14.66	46.03	7.29

EXPERIMENT 18

Discussion

In this experiment the temperature was decreased 150°C, the pressure lowered by 7,500 psi and the time increased to 118 hours. Otherwise the experiment is the same as 16 or 17. Sr^n and $^*Sr^{87}$ losses from the biotite were 46% and 1.3% respectively using the biotite data and 27% and 0.5% respectively using the albite data.

Conclusion

The biotite has lost a maximum of 46% and 1.3% of Sr^n and $^*Sr^{87}$ respectively at the temperature of 450°C in 118 hours.

Table 3-14. Data on Experiment 20

(1) Components: 1.9003 grams Biotite 3138 (-100, +120)

0.8510 grams Albite (-60, +100)

~0.5 ml. demineralized water

(2) Conditions: 450°C, 15000 psi, 190 hours.

(3) Results:

	Before				After	
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.16	5.11 ± 0.04	5.23	16.68	5.14
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.781	20.02	0.14

(4) Sr Migration

	Before				After		
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.23 μgms.	0.02	0.25	0.12	0.09	0.21	0.04
Sr^{86}	3.99	0.31	4.30	2.16	1.67	3.83	0.47
Sr^{87}	2.83	0.22	3.05	1.54	1.18	2.72	0.33
Sr^{88}	33.41	2.63	36.04	18.11	13.97	32.08	3.96
$*Sr^{87}$	9.71	0.08	9.79	9.77	0.13	9.90	-0.11
Total	50.17	3.26	53.43	31.70	17.04	48.74	4.69

EXPERIMENT 20

Discussion

This experiment is the same as 18 except for the length of time involved. Using the biotite data the Sr^n and $^*Sr^{87}$ losses were 48% and -0.7%. With the albite data the same values are 34% and 0.5%.

Conclusion

The biotite has lost a maximum of 48% Sr^n and 0.5% $^*Sr^{87}$ at 450°C in 190 hours.

Table 3-15. Data on Experiment 21.

(1) Components: 1.8998 grams Biotite 3138 (-100, +120)

0.8510 grams Cleavlandite (-60, +100)

~0.5 ml. demineralized water.

(2) Conditions: 600°C, 15000 psi, 12 hours.

(3) Results

	Before			After		
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40± 0.16	5.11± 0.04	4.93	17.32	5.09
Cleavlandite	0.9454	3.82± 0.03	0.08± 0.01	0.806	17.35	0.16

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.23 µgms.	0.02	0.25	0.13	0.08	0.21	0.04
Sr^{86}	3.99 "	0.31	4.30	2.29	1.44	3.73	0.57
Sr^{87}	2.83 "	0.22	3.05	1.63	1.02	2.65	0.40
Sr^{88}	33.40 "	2.63	36.03	19.18	12.08	31.26	4.77
$*Sr^{87}$	9.71 "	0.08	9.79	9.67	0.14	9.81	-0.02
Total	50.16 "	3.26	55.42	32.90	14.76	47.66	5.76

EXPERIMENT 21.

Discussion

To complete the picture at 600°C and 15000 psi a run was performed for 12 hours, compared to experiments 16 and 17 of time intervals 45 and 112 hours respectively. The Sr^n and $^*Sr^{87}$ losses are 43% and 0.5% for the biotite data, and 30% and 0.6% using the albite data.

Conclusion

The biotite has lost a maximum of 43% Sr^n and 0.6% $^*Sr^{87}$ at 600°C in 12 hours.

Table 3-16. Data on Experiment 22.

(1) Components: 0.8478 grams of Biotite 3138 (-100, +120)

1.8987 grams of Cleavlandite (-60, +100)

~0.5 ml. demineralized H_2O

(2) Conditions: 600°C, 15000 psi for 12 hours.

(3) Results.

	Before				After	
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.16	5.11 ± 0.04	6.37	14.16	5.07
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.848	7.97	0.11

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.10 μgms.	0.04	0.14	0.04	0.08	0.12	0.02
Sr^{86}	1.78 "	0.70	2.48	0.76	1.49	2.25	0.23
Sr^{87}	1.26 "	0.50	1.76	0.54	1.06	1.60	0.16
Sr^{88}	14.91 "	5.86	20.77	6.37	12.49	18.86	1.91
$*Sr^{87}$	4.33 "	0.15	4.48	4.30	0.21	4.51	-0.03
Total	22.38 "	7.25	29.63	12.01	15.33	27.34	2.29

EXPERIMENT 22

Discussion

In this experiment the proportions of biotite/albite were reversed, to see if increasing the proportion of acceptor phase would cause a greater movement of Sr from the biotite. So that this could be compared with a previous run, it was performed under the same T-P-time conditions as experiment 21. The movement of Sr^n and $^*Sr^{87}$ using the biotite data is 43% and 1%. With the albite data it is 41% and 1.4% respectively for Sr^n and $^*Sr^{87}$.

Conclusion

The biotite has lost a maximum of 43% Sr^n and 1.4% $^*Sr^{87}$ at 100°C in 12 hours.

Table 3-17. Data on Experiment 23

(1) Components: 1.9026 grams of Biotite 3138 (-100, +120)

0.8550 grams Cleavlandite (-60, +100)

Solution D: ~0.8 ml. aqueous solution containing

41 μgms K^+/ml.

(2) Conditions: 600°C, 15000 psi, 45 hours.

(3) Results.

	Before				After	
Component	$(Sr^{87}/Sr^{86})_N$	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138	3.192	26.40 ± 0.22	5.11 ± 0.04	5.36	16.36	5.09
Cleavlandite	0.9454	3.82 ± 0.03	0.08 ± 0.01	0.807	21.45	0.20

(4) Sr Migration

	Before			After			
Isotope	Biotite	Albite	Total	Biotite	Albite	Total	Loss
Sr^{84}	0.23 μgms.	0.02	0.25	0.12	0.10	0.22	0.03
Sr^{86}	3.99 "	0.32	4.31	2.10	1.79	3.89	0.42
Sr^{87}	2.84 "	0.22	3.06	1.49	1.27	2.76	0.30
Sr^{88}	33.45 "	2.64	36.09	17.61	15.00	32.61	3.48
$*Sr^{87}$	9.72 "	0.07	9.79	9.68	0.17	9.85	-0.06
Total	50.23 "	3.27	53.50	31.00	18.33	49.33	4.15

Table 3-18. Data on Experiment 24.

(1) Components: 1.9176 grams Biotite 3138A (-120, +140)

Solution E: ~1.20 ml aqueous solution containing

1030 μgms K/ml

(2) Conditions: 600°C, 15000 psi for 12 hours

(3) Results:

	Before			After		
Components -	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)	(Sr^{87}/Sr^{86})	Total Sr(ppm)	$*Sr^{87}$ (ppm)
Biotite 3138A	N.D.	40.09	5.35	N.D.	33.76	5.35

EXPERIMENT 23 and 24

Discussion

These two experiments were performed at the same T-P conditions and for comparable lengths of time as experiments 16, 17 and 21. The difference comes in the aqueous phase. In experiment 22, using both biotite and albite, the concentration of K was 41 μgms/ml. In experiment 24, only a biotite, B3138A, was used. The aqueous solution contained 1030 μgms K/ml. B3138A is the biotite used before, but is of a different size fraction and of a different purity. The K solutions were used to see if an exchange process could be achieved between the K in the solution and $^*Sr^{87}$ in the biotite. Both experiments present the same results. Some Sr^n has been lost from the biotite but the K solution had no observable effect on the $^*Sr^{87}$.

Conclusion

The K ions in the aqueous phase did not exchange with the $^*Sr^{87}$ ions in the biotite at 600°C in 45 hours.

CHAPTER IV

DISCUSSION OF RESULTS.

1. The System Calcium Plagioclase-Biotite-Solution

(a) Introduction

This system consists of five experiments (2, 4, 5, 6 and 7) which were investigated at the beginning of this study. They are to be considered as preliminary experiments whose purpose is to set up an experimental procedure for further work. Consequently, no one experiment was completely analysed. This means that the results must be considered in a qualitative way. They are included because the trends seen here appear to have a bearing on the results found in the subsequent work.

(b) Discussion

These experiments can be broken down into three subgroups. Experiments (2) and (4) deal with the two phase system plagioclase-solution. Experiment 5 is concerned with the two phase system biotite-solution. Experiments 6 and 7 deal with the three phase system plagioclase-biotite-solution.

The results of the two experiments dealing with plagioclase and Sr solution show quite clearly that the Sr has left the fluid phase and gone to the mineral. The Sr could either be loosely adsorbed onto the grain surface, firmly adsorbed, or it could have entered the crystal lattice as a result of an exchange reaction with either Ca or Na of the plagioclase. To get some idea of which of these three possibilities is the most reasonable, the plagioclase was leached at room temperature in cold demineralized water. The results are summarized in Table 4-1.

Table 4-1.

The Effect of Leaching on the Observed Sr^{84}/Sr^{86} Ratio in Plagioclase

Component	Sr^{84}/Sr^{86}	μgms of Solution B Sr in Plagioclase
(1) Plagioclase, Exp. 4.	0.289	39.2
(2) Plagioclase, Exp.4, leached one hour.	0.276	36.8
(3) Plagioclase, Exp. 4,leached two hours.	0.269	35.8

These results indicate that at least 9% of the Sr which moved to the mineral from the fluid was loosely adsorbed. This fraction was probably added during the quenching process at the completion of the run. As to whether the remaining Sr has actually entered the lattice or not, cannot be stated. It is probably a combination of an ion exchange reaction and firm adsorption in fractures and other imperfections in the grain.

Experiment 5 shows that the Sr has left the fluid phase, this time going to biotite. It has done so to the same extent and in a comparable length of time as in the case of plagioclase. Once again it cannot be stated, with the data at hand, whether the Sr has adsorbed itself on the grain surface or participated in an exchange reaction. However, Gerling and Ovchinnikova (1962) found that at 100°C both Rb and K were removed from a biotite after 9 hours of leaching. The solution used contained 1% of $CaCl_2$. As the geochemistry of Sr and Ca are very similar it seems reasonable to suppose that Sr from Solution B might have exchanged with K, Rb or $*Sr^{87}$ in the biotite.

Experiments 6 and 7 are a combination of experiments 2, 4 and 5. These first three experiments show that Sr leaves the fluid phase and goes to either mineral phase. By combining the two minerals into one experimental system it should be possible to tell which phase the Sr does prefer.

In both experiments 6 and 7 it appears that Sr has moved from the plagioclase to the biotite. This could be either a true migration of the Sr ions or simply contamination of the feldspar grains in the biotite. The latter would be due to incomplete separation of the two minerals following the run. It is probable that the latter is the case, because the data shows that more Sr has moved from the plagioclase in 36 hours than in 181 hours at the same temperature and pressure. Consequently this Sr movement from the plagioclase will be neglected for the purpose of the discussion, and only the Sr migration from the fluid will be considered. Therefore after 36 hours (experiment 7) the partition of Sr from the fluid in favour of biotite is $^{10}/_{2.5} \sim 4$ to 1. After 181 hours (experiment 6) it is $^{12}/_{5} \sim 2.4$ to 1.

It is realized that the above picture of the movement of Sr is a highly simplified version. In all probability, there has been movement of Sr out of the plagioclase and biotite as well as the migration of Sr from the fluid phase to the mineral phases. However, to speculate any further with the data available would be unprofitable.

(c) Conclusion

(1) At 600°C under a pressure of 1000 bars it is evident that Sr prefers either mineral phase to the fluid.

(2) The addition of Sr to either mineral is probably a combination of adsorption and ion exchange reactions.

(3) In the presence of a mineral phase which should accept Sr readily (plagioclase) the Sr from the fluid has instead moved primarily to a mineral phase which does not readily take in Sr (biotite).

2. The System Biotite-Fluorite-Solution

(a) Introduction

Experiment 9, 10 and 12 consists of the biotite 3205, fluorite and demineralized water (9 and 10) or a Ca^{++}-K^{+} solution (12). The mineral fluorite was chosen as an acceptor phase for Sr. This is a Ca mineral and as such should readily take Sr into its structure. Steyn (1954) found that dark purple fluorite contained up to 10,000 ppm Sr and that colourless fluorite contained the least. Allen (1952) found that hydrothermal vein fluorites contain up to 5000 ppm Sr. The fluorite in the present investigation is a colourless vein fluorite. Therefore, it is very definitely undersaturated with respect to Sr, and should accept it readily.

(b) Discussion

Experiments 9 and 10 were carried out at a temperature and pressure outside the stability limits for Fe rich biotites. The low P_{total} (including P_{H_2O}) should cause biotite to dehydrate by giving up its structural water. The high Po_2 should cause extensive oxidation of Fe from the ferrous to the ferric state. This latter is most definitely seen on microscopic examination. The biotite as a whole however, retains its physical appearance, but it is probable that a certain amount of dehydration has occurred.

Looking first at non-radiogenic Sr (the symbol Sr^n will be used from here on) it is seen that the fluorite has increased its concentration by 14% (2.54 μgms) in 97 hours and only 5% (0.83 μgms) in 210 hours at the same T + P. This points out very clearly the problems involved in interpretating any data on Sr^n. This problem will receive a full discussion later.

For $*Sr^{87}$ a more satisfactory picture is seen. In 97 and 210 hours, the fluorite has gained 0.08 and 0.34 μgms respectively. It has had a marked effect on the Sr^{87}/Sr^{86} ratio (Tables 3-6 and 3-7). This correlates with the findings of Compston and Jeffery (1959), Allsopp (1961) and Lanphere et al (1963) where they got Sr^{87}/Sr^{86} values for apatite (another Ca phase with no Rb) of 0.77, 0.74 and 0.88 respectively. Therefore the migration of $*Sr^{87}$ from a Rb rich phase to a Ca phase with no Rb is indeed a reason for the "anomalous common Sr" values as reported by Compston and Jeffery (op. cit.) and others.

By lowering the temperature 100°C (experiment 12) the migration of Sr^n and $*Sr^{87}$ has been effectively stopped (Table 3-8). Only a slight increase in the Sr^{87}/Sr^{86} ratio is noted and is seen to be very minor in comparison to experiments 9 and 10. The drop in temperature could have decreased the energy below a level needed to activate the Sr ions and thus prevented their migrating from the biotite. In addition, the presence of Ca^{++} ions in the solution could have retarded any reaction between the liquid and the Sr ions in the biotite. Kulp and Engel (1963) and Gerling and Ovchinnikova (op. cit.) found that too low a Rb/Ca ratio in an aqueous phase prevented exchange between Rb in the solution and K or Sr in the biotite. The results of the next two experiments, where albite is substituted for fluorite, sheds some light on these problems.

3. The System Biotite-Cleavlandite-Ca^{++}-K^{+} Solution.

(a) Introduction

The purpose of replacing fluorite by albite (cleavlandite) was to study the behavior of one biotite towards two different acceptor phases. This albite is a cleavlandite from a pegmatite. It has a very high Sr^{87}/Sr^{86} ratio for its Rb content and must be secondary in origin. However, this will not affect its use in these experiments i.e. its role as an acceptor of Sr from another mineral.

(b) Discussion

These two experiments (13 and 14) were carried out at the same T + P and contained the same liquid phase as 12. It is obvious that in experiment 13 and 14 the migration of Sr has been much more extensive than in 12. The results of these two experiments show very clearly that the temperature of 650°C is not too low to allow migration of Sr. It also shows that the Ca^{++} ions in the solution do not play a retardation role. This then rules out the two possibilities suggested earlier. Therefore, the rate controlling step is not the migration of Sr from the biotite. The rate is controlled by the nature of the acceptor phase used. This is the only logical explanation that will explain the difference between experiment 12 and 13 or 14.

4. The System Biotite-Cleavlandite-Water.

(a) Introduction

This system was used in the remaining experiments. Numbers 16, 17, 18, 20 and 21 constitute the system proper, while 22, 23 and 24 test various facets of it. It differs from the preceeding system in that a new biotite is being used and the liquid phase has been changed to demineralized, distilled water. Figures 4-1 to 4-6 show graphically the data from Tables 3-11 to 3-15. The lines are for the sole purpose of connecting points of the same temperature.

(b) Discussion

Figure 4-1 shows that Sr^n appears to have reached

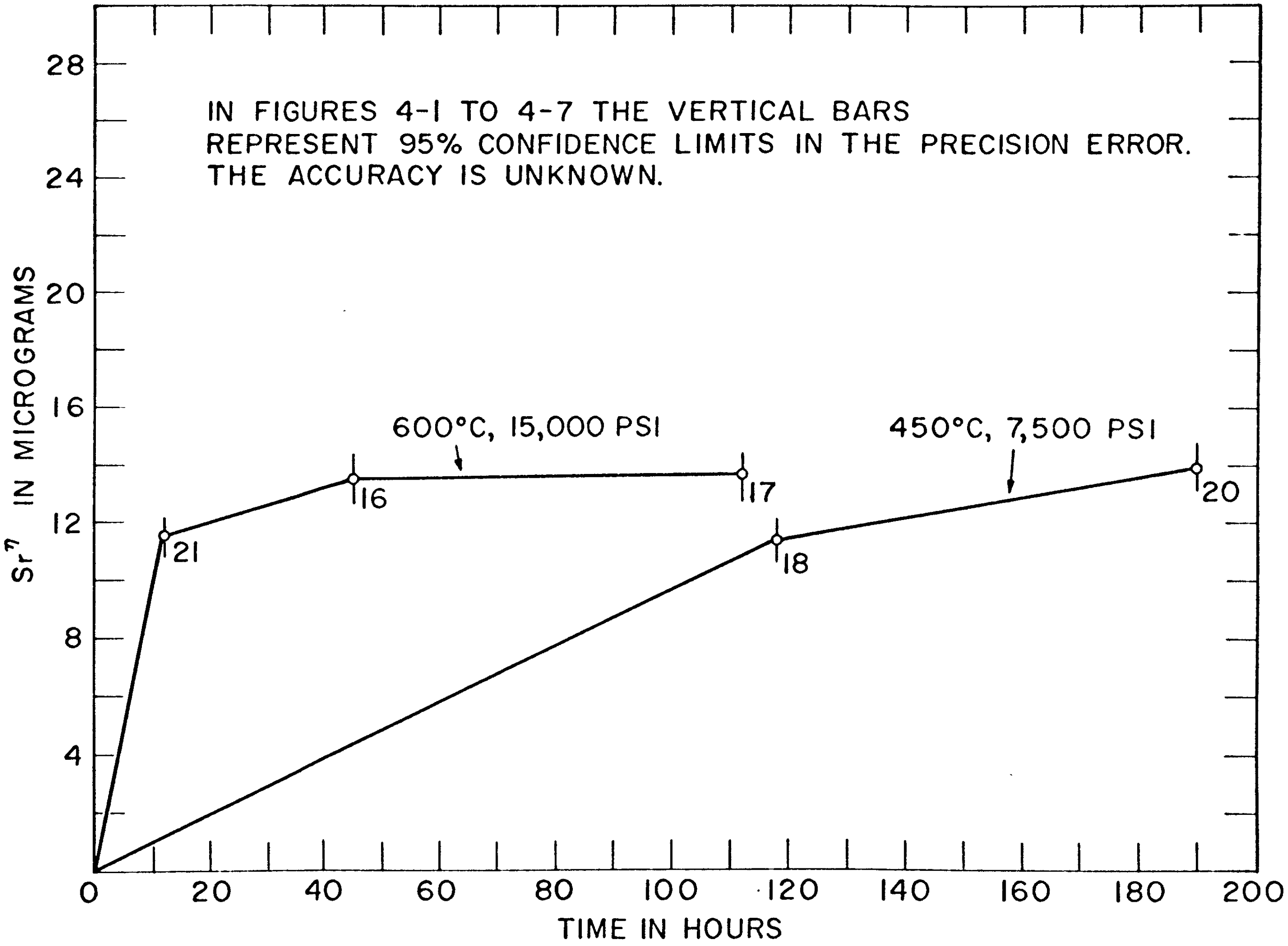


FIGURE 4-1 MOVEMENT OF Sr^{7} FROM BIOTITE 3138 TO ALBITE USING THE ALBITE DATA

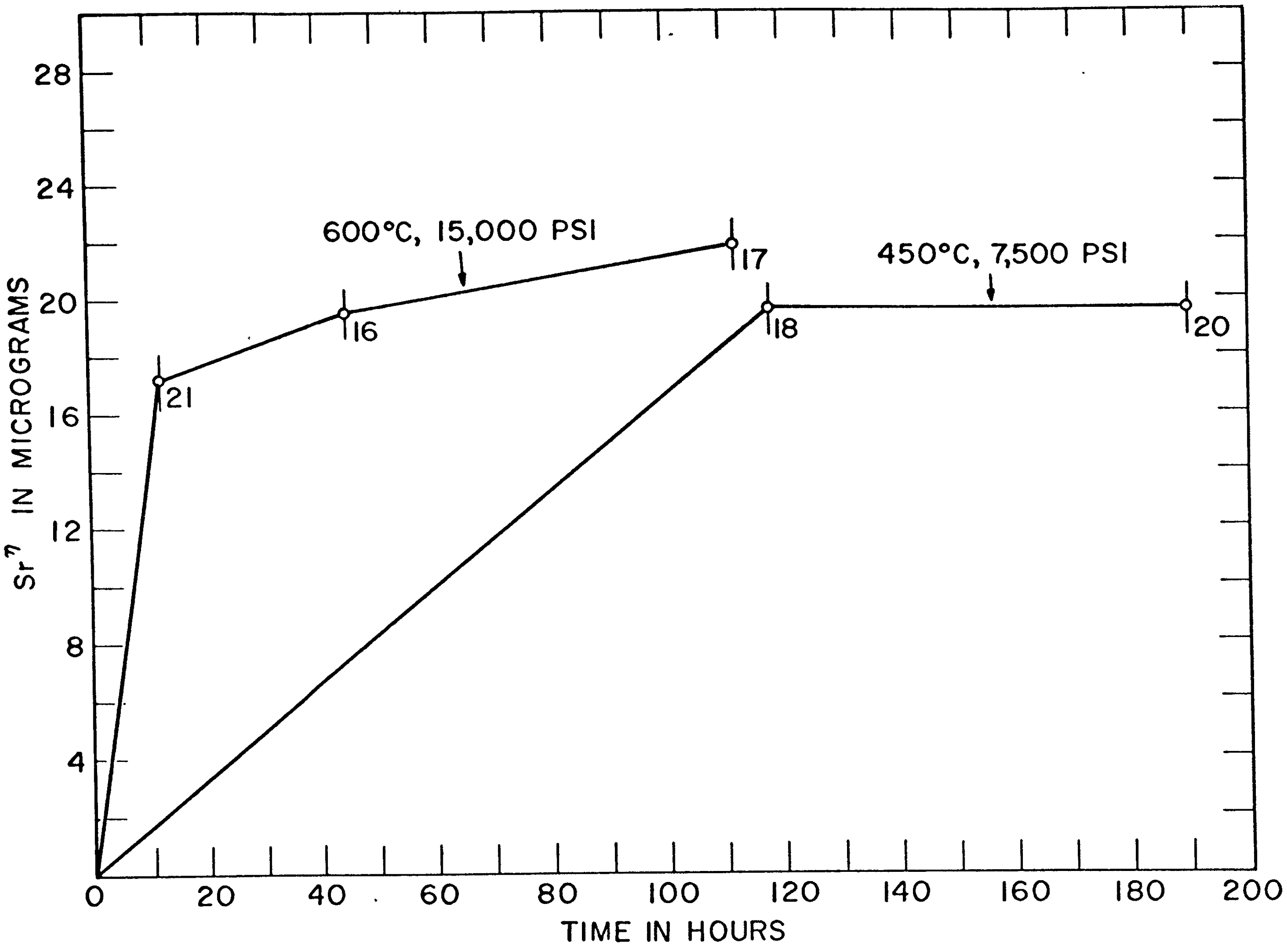


FIGURE 4-2 MOVEMENT OF Sr^{η} FROM BIOTITE 3138 TO ALBITE USING THE BIOTITE DATA

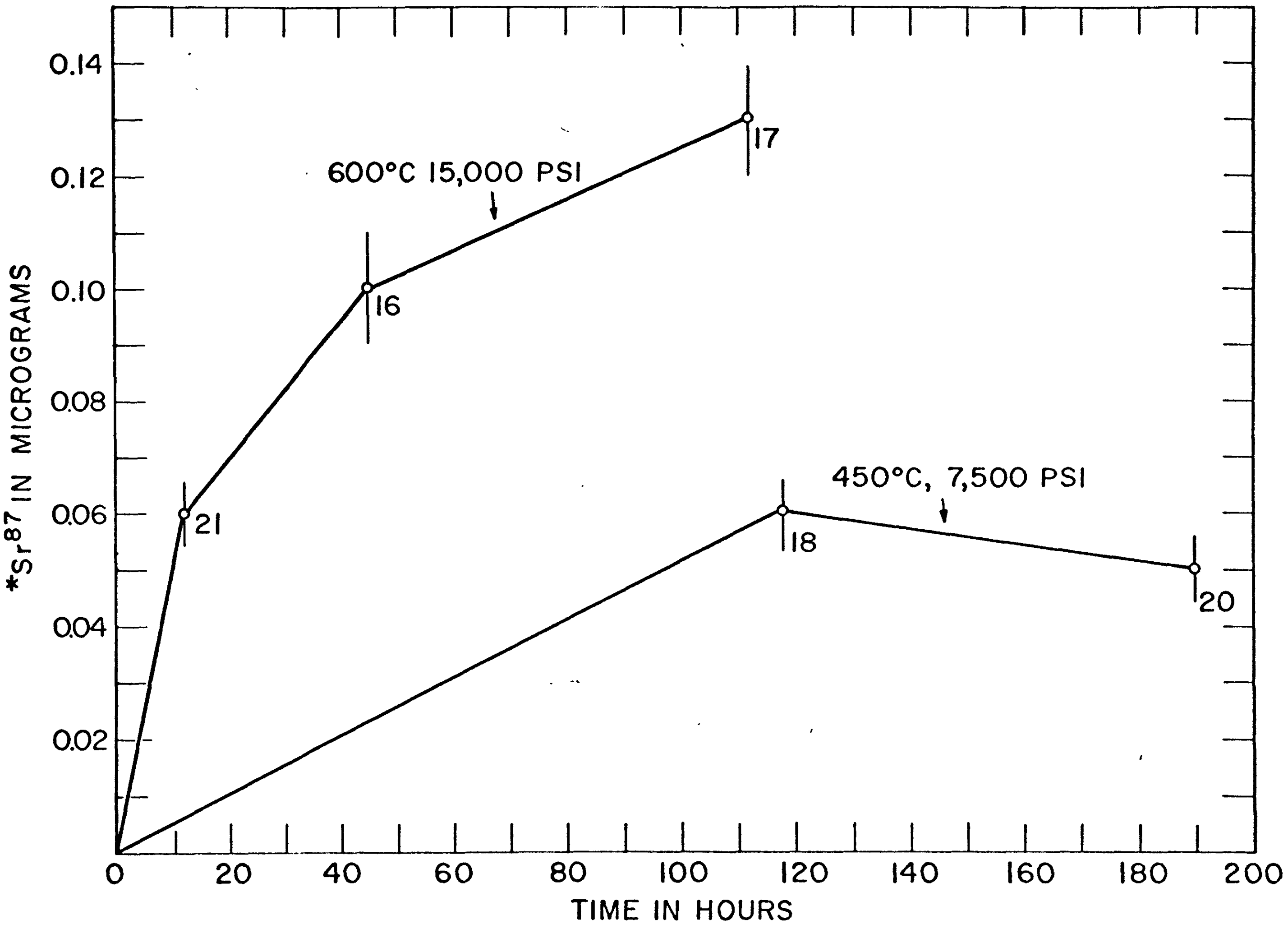


FIGURE 4-3 MOVEMENT OF *Sr^{87} FROM BIOTITE 3138 TO ALBITE USING THE ALBITE DATA

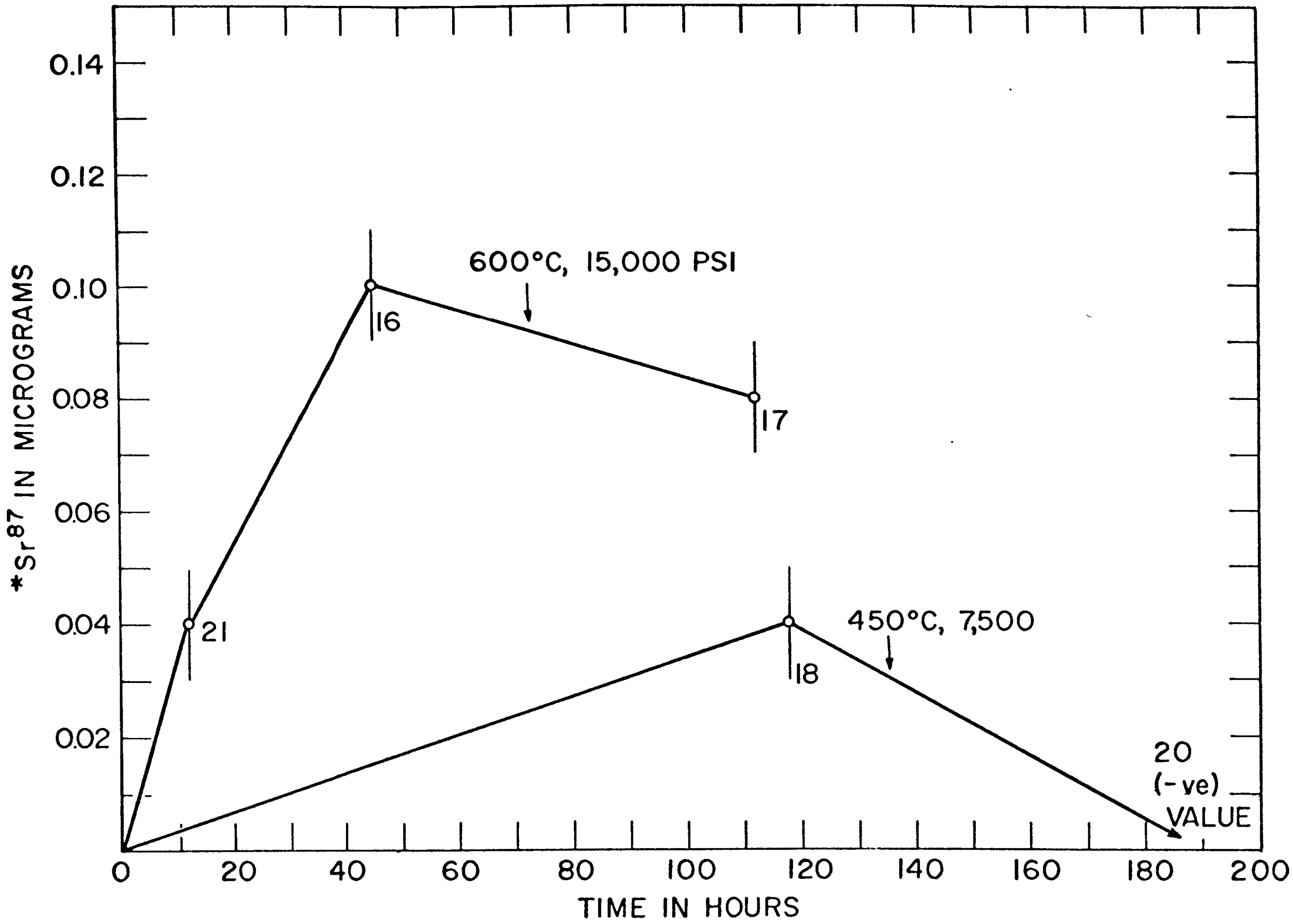


FIGURE 4-4 MOVEMENT OF $^{*}Sr^{87}$ FROM BIOTITE 3138 TO ALBITE USING THE BIOTITE DATA

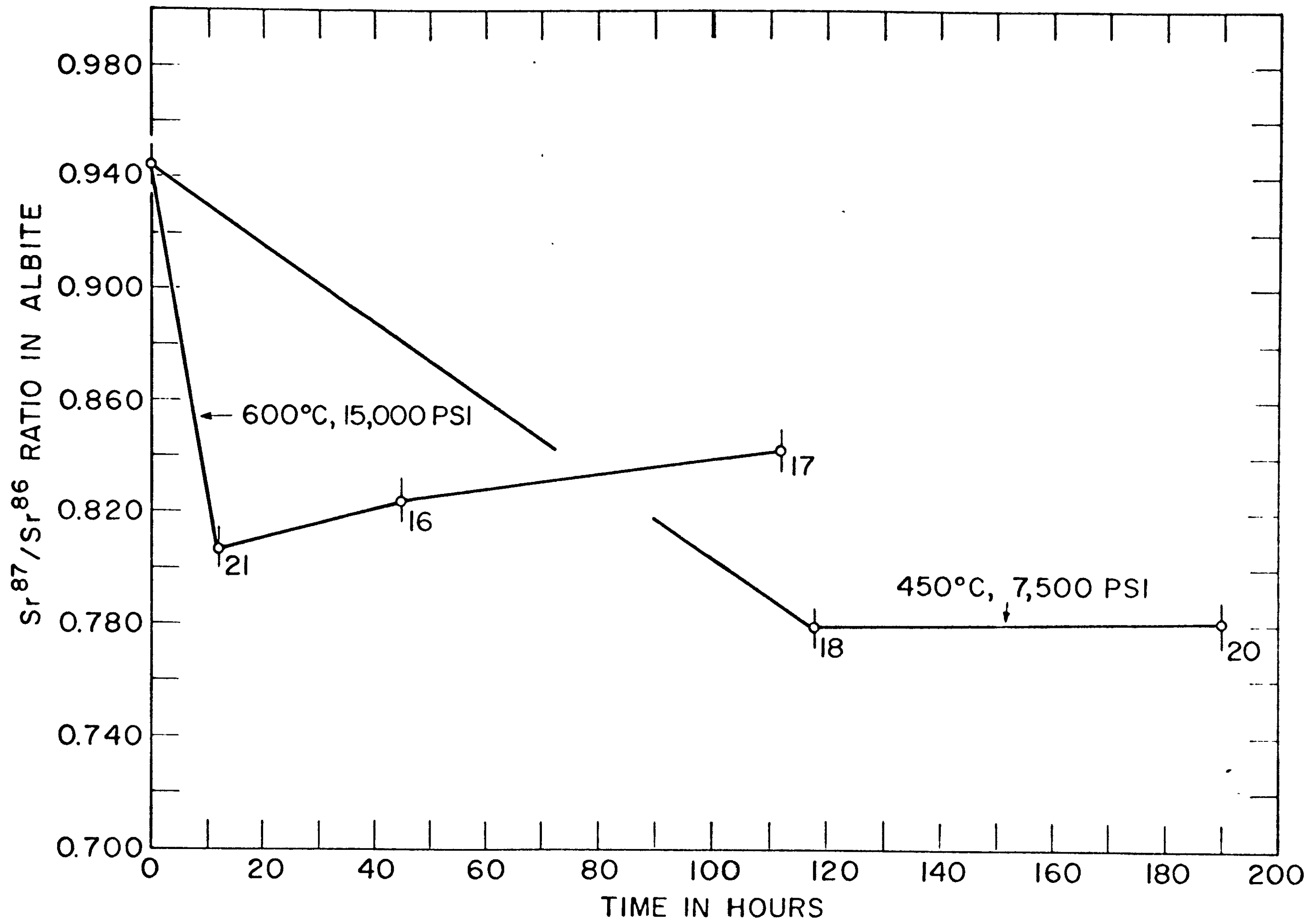


FIGURE 4-5 THE CHANGE IN THE Sr^{87}/Sr^{86} RATIO IN ALBITE WITH TIME

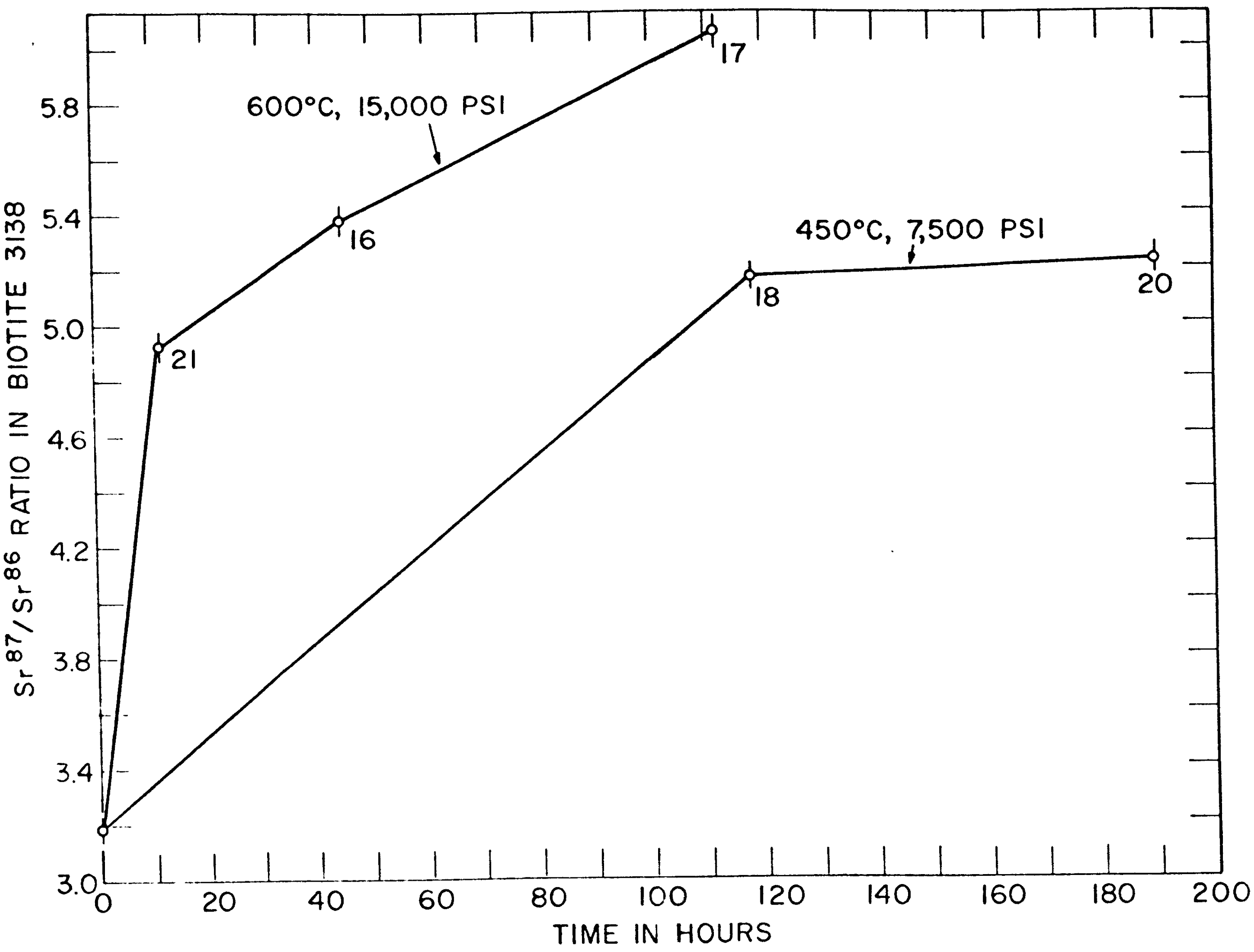


FIGURE 4-6 THE CHANGE IN THE Sr^{87}/Sr^{86} RATIO IN BIOTITE 3138 WITH TIME

an equilibrium value at 600°C. No such definite conclusion can be drawn from the data at 450°C. There is a suggestion of an approach to an equilibrium value, and it will certainly be as great as or greater than the value at 600°C. Looking at Figure 4-2 just the opposite trend is seen, that is, equilibrium at 450°C but not quite at 600°C for Sr^n migration from biotite. Here again is the discrepancy whereby biotite has lost more Sr than the albite has gained.

Figures 4-3 and 4-4 show the movement of $^*Sr^{87}$ in terms of albite and biotite. The albite data shows a consistent picture of increased migration with time and temperature. The biotite data suggests that the migration has ceased at 600°C. At 450°C, the data is confusing and little can be said for it. Therefore it is necessary to consider the albite data as presenting the true picture for $^*Sr^{87}$.

Figures 4-5 and 4-6 show the change in the Sr^{87}/Sr^{86} ratio in both minerals with time. The trends noted for both are explained by saying that Sr^n has moved proportionally faster than $^*Sr^{87}$ thereby increasing the ratio in biotite and decreasing it in albite.

Experiment 22 is a repeat of experiment 16 with the proportions of the two minerals reversed.

Table 4-2 compares the results of these two experiments.

Table 4-2

Comparison of Sr Migration using Reversed Proportions of Albite/Biotite.

Experiment Number	Albite Biotite ratio	Sr^n loss μgms.	Biotite %	$^*Sr^{87}$ loss μgms.	Biotite %
16	0.45	17.3	48	0.10	1.0
22	2.22	7.8	43	0.06	0.8

This experiment shows that by reversing the proportions of albite to biotite an apparent decrease in the migration of Sr^n has occurred. For $^*Sr^{87}$ it is the same percentage wise within experimental error. This will be discussed again in the section on diffusion.

Not much can be added to what already has been said for experiment 23 and 24 (Chapter III). K ions have not exchanged with $^*Sr^{87}$ in the biotite. The loss of Sr^n is due to the same process as in the other experiments and will be discussed next.

5. The Behavior of Sr^n and $^*Sr^{87}$ towards Albite, Fluorite and Fluid.

(a) Introduction

The questions that must be answered before any interpretation can be given to these results are:

1) why will Sr^n and $^*Sr^{87}$ migrate more readily to cleavlandite than fluorite?

2) why does the imbalance of Sr occur only when significant migration has occurred?

3) why does Sr^n migrate more rapidly than $^*Sr^{87}$?

In order to understand any of this, the nature of Sr^n must be determined. It is certain that $^*Sr^{87}$ occurs in the interlayer position of biotite in what was once a Rb site. Based on ionic size alone, Sr (ionic radius = 1.16A° in 8 fold coordination) should also occur in the interlayer position in an undisturbed biotite lattice. It is much too large to occur in the octahedral position with Fe and Mg. However, Sr^n might also occur in inclusions such as apatite and fluorite. In this connection Jäger (1962) found a parallel correlation between the Sr content and impurity content in her biotites. This problem of the location of Sr^n is believed associated with the imbalance found in the Sr analyses. Therefore they will be discussed together.

(b) Test for Sr in the liquid phase and copper jacket.

Following a run, only the mineral phases were analysed. However, Sr might remain in the liquid phase or adsorbed onto the walls of the copper jacket and thus contribute to the imbalance of Sr. The liquid phase and copper jacket were analysed in two cases. The results are given in Table 4-3.

Table 4-3

Data on Sr Analyses of Liquid Phase and Copper Jacket.

Phase	Total Amount of Sr in micrograms
liquid, Experiment 13	0.53
liquid, Experiment 17	0.51
Copper Jacket, Experiment 17	0.03
Copper Jacket, Experiment 22	0.03

From this table it can be seen, that while a certain amount of Sr exists in both phases, it is very minor and can in no way account for the discrepancies noted.

(c) Inclusions

In Appendix A, each of the minerals used in this investigation have been described. In all the biotites inclusions were noted, the main ones being zircon, iron oxide and apatite and/or fluorite. Zircon and iron oxide are of little concern as far as Sr is concerned, but apatite and fluorite, being Ca phases, are serious contaminants. As much as possible, estimates have been made on the volume content of these latter two minerals and it has been placed at less than 1%. However additional experiments were deemed necessary to obtain a better idea of the role that these inclusions might play.

1. Test for phosphorous in Biotite.

The test for P_2O_5 as described by Shapiro and Brannock (1956) was performed on biotite 3138. In this way, an estimate of the content of apatite $[Ca_5(PO_4)_3\ OH,F,CL]$ can be made. Two analyses, one on the untreated biotite and the other on the biotite from experiment 21 <u>both</u> gave a value of 0.09% P_2O_5 by weight. When converted to apatite, this is 0.22% by weight.

2. Analysis of Sr in Apatite and Fluorite.

A mixed sample of apatite and fluorite, taken from the same hand specimen as biotite 3138, was analysed for Sr by X-ray fluorescence using a Mo tube and a topaz analysing crystal. The mixed sample was split into two parts. One portion was placed in a platinum dish on the steam bath. Vycor distilled 2NHCL was added and it preferentially dissolved apatite. The second portion was saved for direct analysis. Grain counting before and after showed the mixed sample to be 96% apatite, 4% fluorite. Furthermore, X-ray analysis showed apatite and fluorite to contain approximately the same concentration of Sr. Therefore the original mixture was analysed using G-1 as a standard. After applying mass adsorption coefficient corrections (Liebhafsky et al, 1960) it was found that apatite contained 180 ppm Sr. This means that the contribution of apatite Sr to biotite would be:

1.000 grams biotite X 0.22% by weight apatite X 180 ppm = 0.4 ppm.

The above shows that apatite itself has little effect on the concentration of Sr in the biotite. However the effect of such phases as fluorite, feldspar, epidote etc. have yet to be evaluated.

3. Heavy liquid Separation of Impurities.

In an attempt to remove most of the above listed impurities, the biotite 3138 was ground to -400 mesh, washed with acetone to free it of dust particles and split into two portions. One portion was saved for direct analysis on the X-ray machine. The second portion was treated with the heavy liquids bromoform and methylene iodide. The methylene iodide was diluted with acetone so that biotite floated while phases such as apatite, fluorite, epidote etc. sank. The float from this process was placed in undiluted bromoform causing biotite to sink and phases such as feldspar to float. In both cases, the -400 mesh powder was centrifuged with the respective liquid for 20-30 minutes. This treatment decreased the peak intensity by approximately 7%. This is not too accurate because the concentration of Sr in biotite is almost at the detection limit of X-ray fluorescence.

This means that in a biotite containing 21 ppm Sr^n (biotite 3138) that 21 X 7% $\sim$ 1.5 ppm is due to foreign sources. This must be considered a minimum value. The extent of inclusions occurring in the micron and several micron size range is not known and is impossible to estimate.

(d) Inhomogeneous Reaction

There does exist the possibility that the sample selected for mass spectrometric analysis is not a true representative of the whole mineral phase used. The portion recovered after the run may be a biased portion of the original amount. In Table 2-2 it can be seen that 2.4% of the total weight of the mineral phases was lost during separation on the magnetic separator, and that 1.3% was lost on the initial recovery from the jacket. This is representative of all the runs. In the majority of the runs (experiments 16-24) both mineral phases were of uniform grain size (-60, +100 for albite, -100, +120 for biotite 3138). To test the efficiency of the magnetic separation, these two mineral phases were weighed, thoroughly mixed, separated and again weighed. They received no hydrothermal treatment. Table 4-4 gives the results and it can be seen that an excellent recovery was obtained.

Table 4-4

Test of Recovery from Frantz Isodynamic Magnetic Separator.

(1) Weight of biotite = 0.8871 grams

(2) Weight of albite = 0.9699 grams

(3) Thoroughly mixed together and passed through the separator at a current of 0.36A, 15° side tilt, 25° forward tilt.

(4) Weight of biotite = 0.8957 grams

Recovery: $\frac{0.8957}{0.8971} \times 100 = 99.84\%$

(5) Weight of albite = 0.9680 grams

Recovery: $\frac{0.9680}{0.9699} \times 100 = 99.80\%$

In three experiments, immediately following the recovery of the minerals from the jacket and before their separation, a sample of the mixture of minerals was taken. This was analysed and compared with the results on the separated mineral fractions. The results are summarized in Table 4-5.

Table 4-5

Comparison of Total Mixture Data with Separated Mineral Data

Experiment Number	Original Sr^n in jacket (μgms)	Recovered (mineral data)	Recovered Total Mixture.
21	43.6 μgms	37.9 μgms	41.0 μgms
16	43.6 "	36.6 "	37.8 "
17	43.6 "	35.3 "	39.5 "

The sample from which the total mixture portion was removed was a mixed combination of albite and biotite with the original grain sizes of -60, +100 and -100, +120 respectively. In addition to the biotite having suffered partial alteration as reported in Chapter III, the grains of this mineral partially broke down to a finer size (approximately 250 mesh). The albite grains did not suffer this effect.

To obtain a representative fraction from a sample varying in grain size from -60 to ~250 mesh is difficult and it is not surprising that the total mixture data does not agree with the original values. The important thing to note in table 4-5 is that the total mixture values are always greater than the separated mineral data. Also, with increasing time (experiment 21 to experiment 17) the discrepancy between the separated mineral values and the original values increases, but this is not the case with the total mixture values versus the original values.

Turning now to table 4-6 it is seen that the results for experiment 21, 16 and 17 are tabulated in a different fashion. The calculations assume that the mass spectrometric analyses are good only for the portion of mineral finally recovered, and not for the original quantities. If however, a homogeneous

Table 4-6

Balance of Sr in Hydrothermal Runs.

A. Mineral Recovery:	21	16	17
(1) Original amount of minerals in Cu jacket	2.7508 grams	2.7472 grams	2.7463 grams
(2) Initial recovery of minerals from jacket	2.7165 "	2.6753 "	2.7093 "
(3) Separated portion for "total mixture" analysis	0.1571 "	0.0980 "	0.0990 "
(4) Final recovery of biotite from Frantz	1.7195 from orig 1.8998	1.7184 from orig 1.8993	1.6238 from orig 1.8984
(5) Final recovery of albite from Frantz	0.7859 from orig 0.8510	0.7735 from orig 0.8479	0.7901 from orig 0.8479
(6) Lost on separation on Frantz	0.0540 grams	0.0254 grams	0.1884 grams
(7) Total loss	0.0883 = 3.2%	0.0973 = 3.5%	0.2334 = 8.5%

Table 4-6 - continued

B. Strontium Recovery	21	16	17
(1) Original quantity	$\frac{43.6\ \mu gms}{2.7508\ grams} = 15.8ppm$	$\frac{43.6\ \mu gms}{2.7472\ grams} = 15.9ppm$	$\frac{43.6\ \mu gms}{2.7463\ grams} = 15.9ppm$
(2) Total mixture	$\frac{2.3\ \mu gms}{.1571\ grams} = 14.9ppm$	$\frac{1.4\ \mu gms}{.0980\ grams} = 13.8ppm$	$\frac{1.4\ \mu gms}{.0990\ grams} = 14.4ppm$
(3) Biotite	$\frac{21.0\ \mu gms}{1.7195\ grams} = 12.2ppm$	$\frac{18.8\ \mu gms}{1.7184\ grams} = 10.9ppm$	$\frac{15.9\ \mu gms}{1.6238\ grams} = 9.8\ ppm$
(4) Albite	$\frac{13.5\ \mu gms}{.7859 grams} = 17.2ppm$	$\frac{15.2\ \mu gms}{1.7735\ grams} = 19.7ppm$	$\frac{15.6\ \mu gms}{.7901\ grams} = 19.8ppm$
(5) Unaccounted for	$\frac{6.8\ \mu gms}{0.0883\ grams} = 77.6ppm$	$\frac{8.2\ \mu gms}{0.0973 grams} = 84.3ppm$	$\frac{10.7\ \mu gms}{.2334 grams} = 45.8ppm$

reaction had occurred between biotite and albite, the Sr loss/mineral loss ratio should give a concentration value in the region of 10-20 ppm. It is obvious that it does not, but in fact gives much higher concentrations.

The only conclusion that can be drawn from this data is that the Sr loss is occurring during separation on the magnetic separator. Furthermore, as the biotite grains have suffered partial breakdown, it is believed that the loss on the separator is primarily biotite. It would be these small grains that would not be recovered on separation. The next question to be answered is why these small biotite grains are so enriched in Sr.

Returning to experiments 2 to 7 it was found that Sr left the fluid phase regardless of whether biotite or plagioclase was present. Also, when both minerals were heated together, the Sr still preferred biotite. Isotope dilution analyses for experiment 6 and 7 showed that biotite probably gained Sr only.

Ieuser (1963) found that Sr left biotite at 600°C and entered the fluid phase. He also commented on the fact that the high temperature distribution of Sr between fluid and mineral returned to STP conditions in minutes i.e. Sr moved back to the mineral. This seems to indicate that the Sr simply adsorbed back onto the mica surface during the quench, and may or may not have returned into the lattice. Probably much the same situation hold in experiment 7. At high temperature, the fluid phase can contain considerable Sr, but not at low temperature. Therefore, it is concluded that part of the reaction noted in these early experiments is due to adsorption on cooling. A certain amount of exchange has undoubtedly taken place, but the fact that Sr from the fluid prefers biotite to a "sink" phase such as Ca plagioclase would suggest that adsorption is certainly playing a role.

Applying this to the system biotite 3138-albite-water it is suggested that the Sr contained in the fluid phase at high temperature adsorbed back onto the grain surfaces during the quenching process. Because of the much greater surface area of biotite in comparison with albite, the major part of the Sr would adsorb back onto the biotite grains. In addition, the biotite has with time further increased its surface area by partial breakdown. These small grains with their very large surface area would adsorb Sr in a disproportionate amount with respect to their weight contribution to the whole biotite sample. This will explain why the discrepancy between mineral values and the original values (table 4-5) increases with time.

(e) Sr Migration to Albite and Fluorite.

As Sr migrates readily to albite, an attempt was made to see how it adhered to the lattice. The albite from experiment 21 was leached at room temperature with five separate aliquots of 6N HCL. The mineral was swirled in each aliquot for 10 minutes before the acid was drained off. The results are seen in table 4-7.

Table 4-7

Results of Leaching on the Albite from Experiment 21.

Albite before leaching = 17.19 ppm Sr^n

Albite after leaching = 16.95 ppm Sr^n

By studying the results in this table it is clear that the Sr added to the albite is held rather firmly. It could be located either in fractures or other grain imperfections, in lattice defects or within the crystal lattice as a result of an ion exchange reaction. It is believed that further leaching experiments will not determine which of the above locations is the true one. Consider the following: if 10% by weight of the albite is dissolved during a leaching experiment and this removed 50% of the Sr, this does not prove that the Sr has simply adsorbed onto the grain surface. In an experimental system such as experiment 21, the Sr would react first with the lattice layers at or near the surface of the grain and only with time migrate to the interior. Therefore, even with a true ion exchange reaction there would exist a greater concentration of Sr near the grain surface than in the interior of the grain. It is this surface or near surface region that would be dissolved in a leaching experiment, thus removing the major part of the Sr and giving the appearance that the Sr had adsorbed onto the grain surface.

Looking now at the two mineral phases albite and fluorite it is obvious that they differ greatly in many respects. Fluorite, CaF_2 has cubic symmetry and a face centered cubic structure with the highest possible coordination (8:4) between the Ca and F ions; Albite, $(Na, Ca)AlSi_3O_8$, has trigonal symmetry and a 3 dimensional tetrahedral framework structure. The cations Na^+, K^+ and Ca^{++} occur in the interstitial channelways or tunnels in this framework. As fluorite is so highly coordinated there exists practically no interstitial space between the ions. Therefore, the only way a Sr ion could enter the lattice is in replacement of Ca. This would require the breaking of an Ca-F bond. For Albite, the Sr could simply migrate into a vacant interstitial position in the lattice and become part of the structure without forcing another ion to leave. At $750^{\circ}C$, it is possible that sufficient energy was obtained to break Ca-F bonds in fluorite and thereby allow Sr substitution.

The most striking phenomena of the movement of Sr, particularly in the systems biotite-albite, is the much faster rate of migration of Sr^n than $*Sr^{87}$. Sr^n could reside in three places in the biotite:

(1) the interlayer position
(2) in inclusions
(3) in the octahedral cation position

(1) The interlayer position

As mentioned earlier, Sr^n should reside in the interlayer position of an undisturbed biotite lattice in the same position as $*Sr^{87}$. Both types of Sr should then show the same pattern of migration. If anything $*Sr^{87}$ should migrate faster. This is the presently held view, i.e. $*Sr^{87}$, a small ion in a large Rb site, is out of equilibrium with the mineral that it is associated with and therefore should migrate readily.

(2) Inclusions.

The Sr^n that has migrated could either have diffused from the inclusions or been released when the inclusions dissolved. It was seen earlier that biotite 3138 analysed after an experiment contained the same P_2O_5 content as the untreated mineral. This suggests that at least apatite has not dissolved extensively during the course of the run. The effect of H_2O as a dissolving agent at higher temperature is not known. The dielectric constant decreases tremendously therefore suggesting that its effect is greatly diminished. If the inclusions have not dissolved, then for Sr^n to leave would require diffusion. Nothing is known about the diffusion properties in these minerals (apatite, fluorite, etc.) so little can be said.

(3) Octahedral position

If Sr^n has not come from inclusions there remains the interesting possibility that it resides in the octahedral position. Based on ionic size it does not belong there and it is probably true that in an undisturbed biotite lattice it does not. However, if a biotite has suffered regional or thermal metamorphism in which migration of ions occurred, it might be possible that the Sr has entered into the octahedral position when the mica lattice was distorted. All three biotites used here are Precambrian in age and have most likely suffered metamorphism. If this is the case, the Sr^n ions are jammed in and should be held rather tightly. But changes have occurred in the octahedral position. Fe^{+2} has oxidized to Fe^{+3} and apparently migrated out of the octahedral position. This is based on the observation that a large increase in the quantity of opaque material (iron oxides) is noted following a run. During this attack on the octahedral position it is possible that Sr^n has drained from this site and migrated to albite. This could be represented by a reaction such as:

$$\text{Sr plagioclase molecule in biotite} \xrightarrow{O_2} \text{Albite}$$

In this connection, Eugster (1959) found that at a T of 600°C and a Po_2 of 10^{-19} atmospheres, Annite broke down in the following way:

$$\text{Annite} \longrightarrow \text{Magnetite} + \text{Sanidine} + \text{Vapour}$$

He found that the same reaction occurred at 750°C at a Po_2 of 10^{-17} atmospheres. The experimental systems used in this investigation have a far higher Po_2 than Eugster's system. However, it must be pointed out here that to form sanidine requires K ions from the interlayer position. If this is the process, (i.e. feldspar cations from interlayer position) the $*Sr^{87}$ should also be liberated. Therefore it is necessary for the experiments biotite-albite-fluid to state that if the Sr^n is coming from the octahedral position, it is the result of a process that has not extensively affected the interlayer position in biotite.

In conclusion all that can be stated is that the Sr^n that has migrated has probably not come from the interlayer position. It could have been derived from either inclusions in the biotite or from the octahedral position of the biotite lattice.

To summarize section 5 of this chapter the following picture of Sr behavior is suggested.

(1) The Sr^n that has migrated has come mainly from inclusions or from the octahedral position in the biotite lattice. If Sr^n has migrated from the interlayer position, it would do so at the same rate as $*Sr^{87}$. As very little $*Sr^{87}$ has moved, the Sr^n from the interlayer position would not be noticed in comparison to the Sr^n coming from other sources.

(2) The reason for the marked difference in behavior of Sr toward albite and fluorite is due to the nature of these two minerals. Sr is able to enter the albite lattice without necessarily affecting an ion exchange reaction, while this is not possible with fluorite.

(3) The loss of Sr during the reaction is probably due to a combination of disproportional adsorption of Sr on the fine grained fraction of biotite because of its increased surface area. This fine grained fraction is then lost on separation. Also, part of the loss might be due to inclusions freed during the time interval of an experiment and lost on separation due to their fine grain size.

(4) If the Sr^n has come from the octahedral position in the biotite, it was freed during some kind of chemical reaction which affected this site but not the interlayer position. It is associated in some way with the oxidation of Fe.

(f) Diffusion

The study of diffusion is based on Ficks Law. It can be stated in two ways:

$$P = -D \frac{\partial c}{\partial x} \qquad (1)$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (2)$$

Equation (1) gives the flux P in the steady state of flow through a unit cross section area, in terms of the concentration gradient and a constant D, the diffusion coefficient. Equation (2) refers to the non stationary state of flow. It describes the accumulation of matter at a given point in a medium as a function of time. This latter form is easily applied to various diffusion models.

If a homogeneous phase of uniform initial concentration and uniform concentration at the surface is assumed, then it is possible to obtain solutions to Ficks' Law for a sphere, cylinder, and slab (Carslaw and Jaeger, 1958, Barrer, 1941). These solutions are further simplified if the surface concentration is taken equal to zero. The most convenient way to express the equations is in terms of F, the fraction lost from the mineral at anytime t.

(1) Slab - this applies to an infinite slab or a slab with impermeable edges.

$$F = 1 - \frac{8}{\pi^2} \sum_{N_{odd}} \frac{1}{n^2} \exp\left[\frac{-n^2\pi^2 Dt}{4\ell^2}\right]$$

where ℓ = half thickness of the slab. For $F < 0.03$ this series can be approximated by:

$$\frac{D}{\ell^2} \simeq \frac{7.76\ F^2}{\pi^2 t}$$

(2) Cylinder - this refers to a cylinder of infinite length or with finite length having impermeable ends:

$$F = 1 - \sum_{1}^{\infty} \frac{4}{\mu_o^2} \exp\left[\frac{\mu_o^2 Dt}{a^2}\right]$$

where a is the radius of the cylinder and μ_0 are the roots of the Bessel function of the first kind and zero order. For $F < 0.02$, this can be approximated by:

$$\frac{D}{a^2} \simeq \frac{1.945 F^2}{\pi^2 t}$$

Sphere:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2\pi^2 Dt}{a^2}\right)$$

where a is the radius of the sphere. If F is small (<0.10) this can be approximated by (Gerling and Morozova 1962):

$$F = \frac{6}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2} t\right)^{\frac{1}{2}} - \frac{3Dt}{a^2}$$

if $F < 0.01$ it can be further approximated to:

$$\frac{D}{a^2} \simeq \frac{0.862F^2}{\pi^2 t}$$

Using these three models and the assumption of zero surface concentration, the D/a^2 values for $*Sr^{87}$ have been calculated for experiments 9-21. The results are listed in table 4-8.

The values as calculated are for the specific systems biotite-albite and biotite-fluorite. They are not considered to represent D/a^2 values for $*Sr^{87}$ diffusion from biotite for any system except the ones investigated during the course of this study. The reason for this is obvious from the preceeding discussion on Sr behaviour towards albite and fluorite.

Table 4-8

Values of D/a^2 for $*Sr^{87}$ (in 10^{-10} sec^{-1}) using Three Models

Biotite 3138 in Experiment	Slab	Cylinder	Sphere
21	7.0	1.7	0.76
16	5.0	1.3	0.58
17	3.5	0.9	0.23
18	0.7	0.16	0.08
20	0.3	0.08	0.03
Biotite 3205 in Experiment			
9	32	8.1	4.5
10	91.0	23.0	11.0
13	120	31.0	14.0
14	16	4.1	1.8
12		0.8	

At 600°C (21, 16, 17): Average Slab = 5.2×10^{-10} sec^{-1}
" Cylinder = 1.3×10^{-10} sec^{-1}
" Sphere = 0.5×10^{-10} sec^{-1}
At 450°C (18, 20) " Slab = 0.5×10^{-10} sec^{-1}
" Cylinder = 0.12×10^{-10} sec^{-1}
" Sphere = 0.05×10^{-10} sec^{-1}

A precision error of ± 30% is placed on these numbers. This is equal to 2σ or 95% confidence limits. The absolute accuracy is unknown.

The diffusion coefficient D itself cannot be determined, because the diffusion radius is unknown. The radius of the biotite grain itself is known, but this is not necessarily equal to the diffusion radius. The Sr ion may only have moved a few microns in distance before it reached the grain surface or a lattice imperfection and thus readily escaped. Therefore, it is necessary to deal with D/a^2.

The activation energy involved in the diffusion of $^*Sr^{87}$ can be determined by use of the Arrenhius equation:

$$\frac{D}{a^2} = \frac{D_o}{a^2} e - \frac{E_{act}}{RT} \quad ,$$

where a = diffusion radius

$\frac{D_o}{a^2}$ = a constant, the frequency factor

E_{act} = the activation energy in calories/mole

R = the gas constant = 1.987 calories/mole-degree

T = the temperature in degrees Kelvin

By plotting $\log_{10} D/a^2$ versus $1/T$, the E_{act} is determined from the slope of the line (equal to $-\frac{E_{act}}{2.303R}$). The data in Table 4-8 have been treated in this way and the results are seen in figure 4-7.

On the basis that Sr^n in the biotite and albite have Sr^{87}/Sr^{86} ratios of 0.710, the E_{act} for the diffusion of $^*Sr^{87}$ from biotite 313S to albite is 20 Kcal/mole in the temperature range 600°-450°C. This calculation

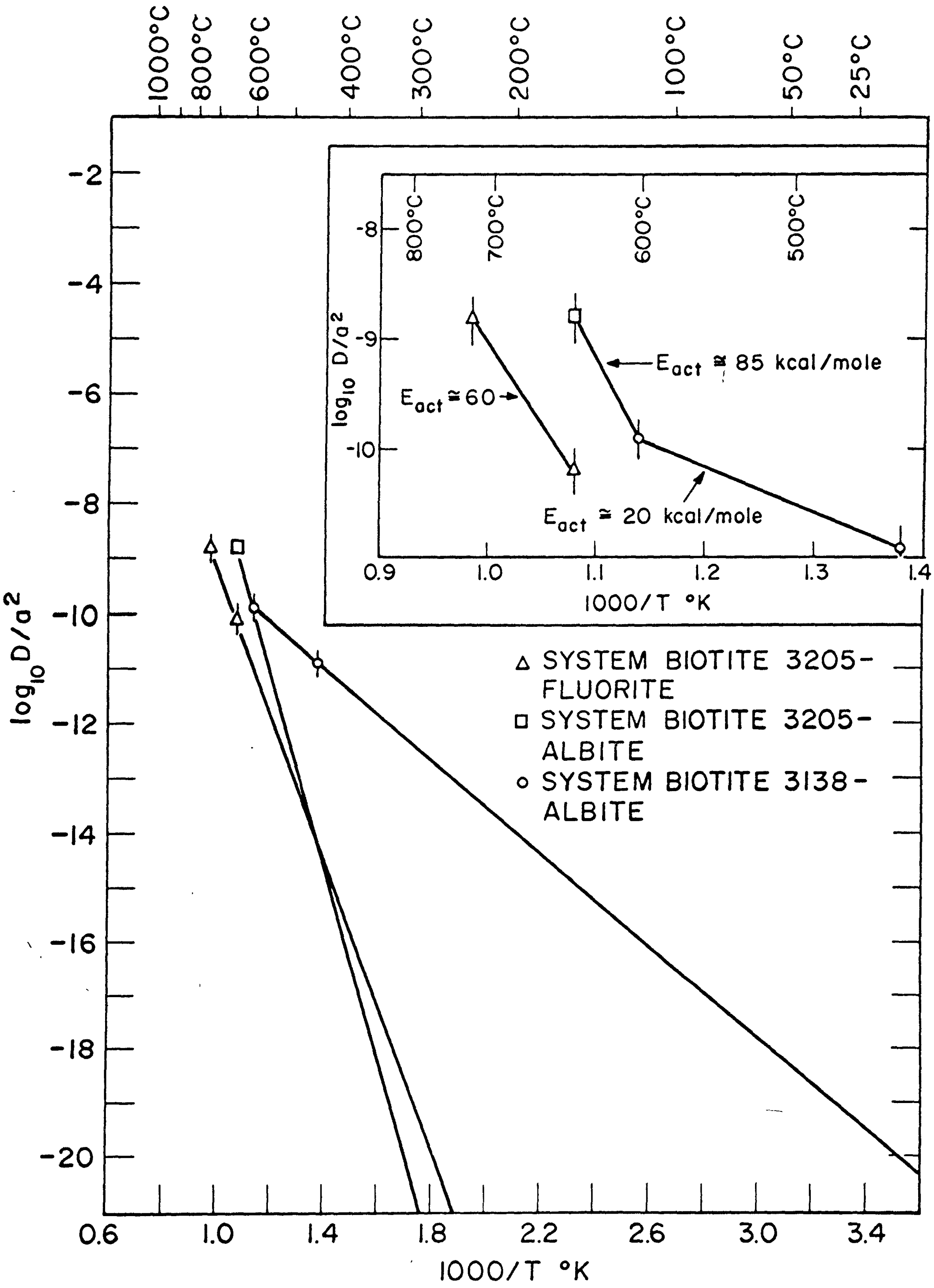


FIGURE 4-7 LOG$_{10}$ D/a^2 vs 1000/T °K

is based on the cylindrical model believed to be the best approximation to biotite.

A line is seen connecting the data for 650°C with that for 600°C. It must be remembered that two different biotites are involved here, biotite 3205 at 650°C and biotite 3138 at 600°C. However, if the discussion is restricted to the migration of $*Sr^{87}$ from the biotite interlayer position, then it is believed that these two biotites can be considered as one. Looking at figure 4-7 it is seen that a much higher E_{act} of 84 Kcal/mole exists between 650°-600°C than in the temperature range 600-450°C. An E_{act} of 60 Kcal/mole is found for the system biotite 3205 - fluorite in the temperature range 750-650°C. The E_{act} for this system is less in value than that for migration at 650-600°C. However, notice that the D/a^2 value for $*Sr^{87}$ diffusion from biotite 3205 to fluorite is the same at 750°C as the D/a^2 for biotite 3205 to albite at 650°C. This is compatible with what was concluded earlier. That is, Sr migrates at a faster rate to albite than to fluorite.

By knowing the E_{act} values it is now possible to determine the time-temperature-D/a^2 relationships as they might apply in geological circumstances. For example, in table 4-9 the temperatures required for 2% loss and 50% of $*Sr^{87}$ from biotite in 1 m.y., 100 m.y., and 1 b.y. are listed. The values given are calculated on the basis of volume diffusion, using the cylindrical model and with the E_{act} values of 20, 60, and 84 Kcal/mole.

An attempt was made to determine a maximum value for the Sr^{87}/Sr^{86} ratio of Sr^n in biotite 3138 and 3205 to see to what degree this ratio might vary from 0.710. By knowing the total Sr content in albite before the run and the total content following the run, it was possible to determine the <u>average</u> Sr^{87}/Sr^{86} ratio of the migrating Sr in the time interval of the run. The results of the calculations are seen in table 4-10.

For the system biotite 3138-albite-water the minimum value is found to be 0.75 (experiment 20). For the system biotite 3205-albite-water it is 1.1. This latter system was run at such a temperature that $*Sr^{87}$ certainly was migrating. Therefore this value is not of much use. In experiments 13 and 17 the fluid phase was analysed for its Sr^{87}/Sr^{86} ratio. For experiment 13 (with biotite 3205) it is approximately 0.76 and in experiment 17 (with biotite 3138) it is approximately 0.74. These values must represent the <u>maximum</u> Sr^{87}/Sr^{86} ratios of Sr^n for these two biotites. The minimum value would be in the range of 0.705 to 0.710. These are the closest limits that can be placed on these values. All discussions in this thesis on the diffusion

Table 4-9

Temperature at which 50% and 2% of $^*Sr^{87}$ would be lost from Biotite in times of one million, one hundred million and one billion years.

E_{act}(Kcal/mole)		2% loss of $^*Sr^{87}$			50% loss of $^*Sr^{87}$		
		1 m.y.	100 m.y.	1 b.y.	1 m.y.	100 m.y.	1 b.y.
(1)	20	80°C	25°C	-	170°C	95°C	60°C
(2)	60	340°C	290°C	265°C	430°C	360°C	335°C
(3)	85	360°C	320°C	300°C	430°C	375°C	360°C

(1) Corresponds to the experimental system biotite 3138-albite in the temperature range 600-450°C.

(2) Corresponds to the experimental system biotite 3205-fluorite in the temperature range 750-650°C.

(3) Corresponds to the experimental system biotite 3205-albite in the temperature range 650-600°C.

Table 4-10

Summary of Results for Albite and Fluorite on Sr Migration in Terms of the Isotopes: Sr^{86}, Sr^{87} and Sr^{88}

Exp. No.	Initial Sr (μgms)			Final Sr (μgms)			Difference = Migrated Sr			
	86	87	88	86	87	88	86	87	88	87/86
10	1.55	1.10	12.99	1.63	1.50	13.68	0.08	0.40	0.67	5.0
13	0.37	0.34	3.09	1.53	1.58	12.79	1.16	1.24	9.70	1.1
14	0.37	0.34	3.09	1.56	1.69	13.09	1.19	1.35	10.00	1.1
18	0.31	0.29	2.62	1.43	1.15	12.00	1.12	0.86	9.38	0.77
20	0.31	0.30	2.63	1.67	1.31	13.97	1.36	1.01	11.34	0.75
21	0.31	0.30	2.63	1.44	1.16	12.08	1.13	0.86	9.45	0.76
16	0.31	0.29	2.62	1.65	1.34	13.80	1.34	1.05	11.18	0.78
17	0.31	0.29	2.62	1.65	1.37	13.84	1.34	1.08	11.22	0.81

of $*Sr^{87}$ will be based on an Sr^{87}/Sr^{86} ratio of Sr^n equal to 0.710. But it must be kept in mind that it could indeed be higher than this value.

As the ratio of 0.710 is assumed for Sr^n in these biotites, the D/a^2 values calculated here must represent maximum values, i.e. minimum E_{act} values, to be found in the experimental systems. If the value of 20 Kcal/mole for E_{act} is applied to temperature-time conditions in the earth, it is seen that significant $*Sr^{87}$ loss from biotite could occur over geologic time without the help of a thermal event at some time subsequent to the mineral's formation. For example, in 1 b.y. at a temperature of 60°C, 50% of the $*Sr^{87}$ could be lost from biotite. This implies that all Precambrian biotite should show significant $*Sr^{87}$loss. However, the data for the systems biotite 3205-albite and biotite 3205-fluorite suggest that a thermal event is indeed needed for any significant $*Sr^{87}$ migration to occur. The incompatability of these latter results with the system biotite 3138-albite necessitates a further look at the cause of $*Sr^{87}$ loss from biotite in the temperature range 600-450°C.

Looking at figure 4-3 once again it appears that the movement of $*Sr^{87}$ is reaching a "plateau" value in the region of 0.15-0.20 μgms. This could represent an approach to an equilibrium situation in which Sr partitions itself between biotite and albite. For Sr^n (figure 4-1) this appears to have occurred after 45 hours. Therefore if a true equilibrium situation for Sr is being established in albite at 600°C then $*Sr^{87}$ migration should cease after 45 hours. This is not the case and suggests that equilibrium has not been reached in the experimental system in the time allowed.

The appearance of equilibrium is due to the rapid movement of Sr^n from some impurity in or from the octahedral position of the biotite as discussed earlier. This movement ceases after 45 hours, but in the interval 45-112 hours Sr^n and $*Sr^{87}$ continue to migrate from the interlayer position. However the quantity is so small in comparison to the quantity added to the albite from the impurities etc., that it causes little difference to the value obtained for the total Sr moved.

It is suggested, but not proved, that the $*Sr^{87}$ migrating from biotite to albite in the temperature range of 600-460°C with an E_{act} of 20 Kcal/mole is coming from the grain surface, grain imperfections or some crystal defect. This represents a desorption process rather than volume diffusion and corresponds to the low temperature loss of Ar from mica as found by Amirkhanoff et al (see page 4 chapter I for references). If the plateau value of 0.15-0.20 μgms is correct this means that about 2% of the $*Sr^{87}$ in biotite 3138 is residing in locations other than the interlayer position of the biotite. That desorption at lower temperatures could be the case is further suggested by the "knee" in the $\log_{10} D/a^2$ versus 1/T plot (figure 4-7) occurring between 650° and 450°C for the system biotite-albite. The slope of the line between 600°C and 650°C may represent more closely E_{act} values necessary for true volume diffusion of $*Sr^{87}$ from the interlayer position in biotite.

The D/a^2-temperature-time conditions as derived from the data in the temperature range 750-600°C (the systems biotite 3205-fluorite and biotite 3205-albite) are compatible with conditions expected in nature. For example, 50% of the $*Sr^{87}$ could be lost from the biotite in 1 m.y. at a temperature of 430°C, a temperature certainly within the metamorphic range.

One point must be made here which concerns the pressure conditions of the experimental runs (9 to 17 and 21) in the temperature range 600-750°C. The runs at 600°C and 1000 bars pressure (biotite 3138) are within the stability limits of biotite except for the high Po_2 which causes oxidation as noted. At 650°C and 500 bars it is marginal and at 750°C and 200 bars it is outside the stability limits. That is, at these higher temperatures and low total pressure biotite (either 3138 or 3205) should start to lose its structural water. There does exist therefore the strong possibility that the $*Sr^{87}$ being released at high temperature is due in large part to the breakdown of the interlayer position of the biotite. In this connection, Gerling and Morozova (1957) and Saradov(1961) believe that the loss of Ar from the interlayer position in micas will only come about when the mica begins to break down by giving off its structural waters. Also Gerling et al (1963) found that the higher the Fe^{+3}/Fe^{+2} ratio in biotites the lower the E_{act} for the release of Ar. They conclude that the entry of Fe^{+3} into the structure somehow "loosens" it up and makes diffusion easier.

(g) Thermodynamics

At the outset of this investigation it was hoped to apply the laws of Thermodynamics as they might apply to trace element distribution. To apply such laws to either the Sr^n or $*Sr^{87}$ data, the equilibrium values must be known or predictable.

Looking at figures 4-1 and 4-2 it could be stated that at 600°C Sr^n has reached an equilibrium value in albite and at 450°C it has done so in biotite. But at 600°C and 450°C this cannot be stated for biotite and albite respectively. Also, there exists the problem of Sr inbalance in all these experiments. Even more, the original location of the Sr^n that has migrated is uncertain.

For $*Sr^{87}$ it is safe to say that equilibrium has not even been closely approached. It appears that at 450°C $*Sr^{87}$ has ceased to migrate. As stated in the previous section, this probably represents $*Sr^{87}$ from imperfections and not from a Rb site in the lattice. At 600° it is seen that $*Sr^{87}$ is just beginning to move after 112 hours. Certainly part of this $*Sr^{87}$ also is coming from lattice imperfections. In any event, equilibrium of $*Sr^{87}$ between biotite and albite has not been attained in the time allowed.

In the same sense, real equilibrium has not been reached for Sr^n. It is certain that some Sr^n resides in its proper place in the interlayer position, but has not migrated any faster than $*Sr^{87}$. The Sr^n that has migrated is primarily from a different location. As mentioned earlier.the reason that it appears no Sr has migrated between 45 hours (16) and 112 hours (17) is that Sr^n was removed and perhaps completely drained from the unknown location after 45 hours. In the time interval from 45-112 hours Sr^n was still migrating from the interlayer position, but its quantity was so low that it created no noticeable increase.

In conclusion it can be stated that due to kinetic effects, an equilibrium distribution of Sr^n and $*Sr^{87}$ between albite and biotite or between fluorite and biotite has not been achieved in the time allotted.

CHAPTER V

SUMMARY AND CONCLUSIONS.

1. Summary and Conclusions

The early experiments with the system biotite 3086-Ca plagioclase-Sr solution demonstrate clearly the difficulty in determining whether a given movement of Sr from the fluid to the solid phase is a true ion exchange reaction or adsorption. The evidence seems to show that a large proportion of the Sr has simply adsorbed onto the biotite grain surfaces. This is based on the results whereby Sr preferred biotite to a Ca plagioclase, the latter being the obvious phase for Sr.

This adsorption of Sr onto the mica surface is believed connected to the problem of Sr loss during the course of any one experiment. It was concluded that Sr from the fluid phase adsorbed onto the mica flakes during the quenching stage of the experimental procedure. The fine sized mica flakes, produced during the course of the run adsorbed a disproportionate amount of Sr with respect to their weight contribution to the whole biotite sample. These small mica flakes were then lost during magnetic separation and created the imbalance seen in the runs.

The Sr^n which migrated from biotite to either fluorite or albite came primarily from impurities within the biotite grain and/or from the octahedral position of the biotite. Sr^n from the interlayer position was almost certainly migrating as well, but was doing so at the same rate as $*Sr^{87}$, thus its contribution to the total Sr^n that migrated to albite was negligible.

The loss of the majority of Sr^n from the biotite is not believed to be a diffusion controlled process, but is somehow associated with the dissolution of impurities such as apatite and fluorite or with the chemical reactions occurring in the octahedral position in the biotite.

The maximum value of the Sr^{87}/Sr^{86} ratio of Sr^n in biotite 3205 and biotite 3138 was found to be 0.76 and 0.74 respectively. In order that a comparison could be made between these two biotites as regards to $*Sr^{87}$ diffusion, it was decided to use a value of 0.710 for Sr^n. In this way the D/a^2 constants for $*Sr^{87}$ migration from biotite to albite or fluorite have their maximum values.

D/a^2 values for $*Sr^{87}$ movement from biotite to albite and fluorite were determined using the relationships of volume diffusion. They were found to vary from 3×10^{-9} sec^{-1} at $650^{\circ}C$ to 8×10^{-12} sec^{-1} at $450^{\circ}C$. It was suggested but not proved, that the loss of $*Sr^{87}$ in the experimental temperature range of 600-450°C was the result of a desorption process from grain surfaces, grain imperfections and crystal defects in the biotite. It was calculated that approximately 2% of the $*Sr^{87}$ in biotite 3138 occurred in localities other than the interlayer position. The experimentally derived E_{act} and D/a^2 values in the temperature range 600-750°C were found to be compatible with the idea of volume diffusion loss of $*Sr^{87}$ during a thermal event. It was found that 50% of the $*Sr^{87}$ could be lost from a biotite at 430°C in 1 m.y. in a natural rock system similar to the experimental system. It was pointed out that due to the low total pressure and high Po_2 of the experiments carried out in the temperature range 600-750°C, that the $*Sr^{87}$ liberated in these experiments could also have occurred when the biotite partially broke down by giving up its structural water and also during the oxidation of the Fe.

Finally, it was found that the movement of Sr^n and $*Sr^{87}$ depended on the second mineral phase present with the biotite. The movement of Sr from biotite in the presence of an ionic non-silicate phase such as fluorite was slower than in the presence of albite.

2. Suggestions for further work

In the present investigation, three mineral phases were used and for each system an attempt was made to reach equilibrium with respect to Sr distribution among the phases. This proved to be unprofitable. A better approach would be the study of all the mineral phases of a particular rock system, treated hydrothermally two at a time, for a definite time period, without concern for equilibrium. In this way, it should be possible to predict which phases would be most susceptible to losing or gaining Sr during metamorphism. The phases that should be investigated include biotite, muscovite, plagioclase, potassium feldspar, hornblende, pyroxene, apatite, fluorite and epidote.

For hydrous phases, it would be profitable to carry out the experiments under conditions of both stability and instability and study the effect on Sr movement during dehydration or recrystallization. Such studies could lead to knowledge of the location of the Sr in the crystal lattice.

The systems could be studied with a variety of liquid phases and under "dry conditions.

It should also prove profitable to study Sr exchange reactions in various mineral phases under dynamic conditions as reported by Kulp and Engel (1963) on micas.

BIBLIOGRAPHY

Aldrich L. T., Davis G. L., Tilton G. R. and Wetherill G. W. (1956) Radioactive ages of minerals from the Brown Derby Mine and the Quartz Creek Granite near Gunnison, Colorado. J. Geophy. Res. 61, 215-232.

Aldrich L. T. and Wetherill G. W. (1960) Rb-Sr and K-Ar ages of rocks in Ontario and northern Minnisota. J. Geophy. Res. 65, 337-340.

Aldrich L. T., Wetherill G. W., Davis G. L and Tilton G. R. (1958) Radioactive ages of micas from granitic rocks by Rb-Sr and K-Ar methods. Trans. Amer. Geophys. Un. 39, 1124-1134.

Allen R. D. (1952). Variation in chemical and physical properties of fluorite. Am. Min. 37, 910-930.

Allsopp H. L. (1961) Rb-Sr age measurements or total rock and separated mineral fractions from the old granite of the Central Transvaal. J. Geophy. Res. 66, 1499-1507.

Allsopp H. L., Roberts H.R. and Schreiner G. D. L. (1962) Rb-Sr measurements on various Swaziland granites. J. Geophy. Res. 67, 5307-5313.

Amirkhanov K. I., Bartnitskii E. N., Brandt S. B. and Voitkevich G. V. (1959a) The migration of argon and helium in certain rocks and minerals. Doklady Ac. Sci. U.S.S.R. 126, 394-395.

Amirkhanov K. I., Brandt S. D. and Bartnitskii E. N. (1959b) The diffusion of radiogenic argon in feldspars. Doklady Ac. Sci. U.S.S.R. 125, 210-212.

Amirkhanov K. I., Brandt S. B., Bartnitskii E. N. and Voronovskii S. N. (1959c) Diffusion of argon in Sylvite. Geochemistry 6, 653-662

Amirkhanov K. I., Brandt S. B. and Bartnitskii E. N. (1960a) Radiogenic argon in minerals and its migration. Annals N. Y. Acad. Sci. 91, Art 2. 235-275.

Amirkhanov K. I., Brandt S. B. and Bartnitskii E. N. (1960b) Gerling's method of determination of activation energy of radiogenic gases in minerals. Geochemistry 7, 778-782.

Baadsgaard H., Lipson J. and Folinsbee R. E. (1961) The leakage of radiogenic argon from sanidine Geochim. et. Cosmochim. Acta 25, 147-157.

Barrer R. M. (1941) Diffusion in and Through Solids. MacMillan Co., London.

Basset W. A. and Giletti B. J. (1963) Precambrian ages in the Wind River Mountains, Wyoming. Bull. Geol. Soc. Am. 74, 209-212.

Bray J. M. (1942) Minor chemical elements in fluorite from Jamestown, Colorado. Am. Min. 27, 769-775.

Carslaw H. S. and Jaeger J. C. (1947) Conduction of Heat in Solids. Oxford Univ. Press, London.

Compston W. and Jeffery P. M. (1959) Anomalous "common Sr" in granite. Nature 184, 1792-1793.

Craddock C., Gast P. W. Hansen G. N. and Linder H. (1964) Rb-Sr ages from Anarctica. Bull. Geol. Soc. Am. 75, 237-240.

Deer W. A., Howie R. A. and Zussman J. (1962) Rock Forming Minerals, 3 Sheet Silicates 1-30 Longmans Press.

Deer W. A., Howie R. A. and Zussman J. (1962) Rock Forming Minerals, 4 Framework Silicates 1-165. Longmans Press.

Deer W. A. Howie R. A. and Zussman J. (1962) Rock Forming Minerals, 5 Non-Silicates 339-356. Longmans Press.

Deuser W. G. (1963) The effect of temperature and water pressure on the apparent Rb-Sr age of
* micas. Unpublished Phd. Thesis, Penn. State Univ.

Eugster H. P. (1959) Reduction and oxidation in metamorphism. Researches in Geochemistry. 397-426. John Wiley & Sons, New York.

Evan C. R., Steiner J. and Weiner J. L. (1964). Age dating studies on precambrian rocks at Jasper, Alberta. Can. Min. & Met. Bull. 57, 33-36.

Fairbairn H. W., Faure G., Pinson W. H., Hurley P. M., and Powell J. L. (1963) Initial ratio of Sr^{87} to Sr^{86}, whole rock age and discordant biotite in the Monteregian igneous province, Quebec. J. Geophy. Res. 68, 6515-6522.

Fairbairn H. W., Hurley P. M. and Pinson W. H. (1961) The relation of discordant Rb-Sr mineral and whole rock ages in an igneous rock to its time of crystallization and to the time of subsequent Sr^{87}/Sr^{86} metamorphism. Geochim. et Cosmochim. Acta 23, 135-144.

Fairbairn H. W., Pinson W. H., Hurley P. M. and Cormier R. F. (1960) A comparison of the age of coexisting biotite and muscovite in some Paleozoic granite rocks. Geochim. et Cosmochim. Acta 19, 7-9.

Faul H. and Jäger E. (1963) Ages of some granitic rocks in the Vosges, the Schwarzwald and the Massif Central. J. Geophy. Res. 68, 3293-3300.

Faure G. (1961) The Sr^{87}/Sr^{86} ratio in oceanic and continental basalts and the origin of igneous rocks. Unpublished Phd. Thesis, M.I.T.

Faure G., Fairbairn H. W., Hurley P. M. and Pinson W. H., (1962) The age of the nickel irruptive at Sudbury, Ontario. 10th Annual Progress Report for 1962, NYO-3943, U.S. Atomic Energy Commission, Contract At(30-1)-1381, 1-5.

Fechtig H., Gentner W. and Kalbitzer S. (1961) Argonbestimmungen an Kaliummineralien - IX Messungen zu der verschiedenen arten der argon diffusion. Geochim. et Cosmochim. Acta 25, 297-311.

Fechtig H., Gentner W. and Lammerzahl P. (1963) Argonbestimmungen an Kaliummineralien - XII Edelgasdiffusionmessungen an Stein-und Eisen meteoriten. Geochim. et Cosmochim. Acta 27, 1149-1169.

Fechtig H., Gentner W. and Zahringer J. (1960) Argonbestimmungen an Kaliummineralien - VII Diffusionsverluste von argon in mineralien und ihre Aswirkung auf die kalium-argon-altersbestimmung. Geochim. et Cosmochim. Acta 19, 70-79.

Folinsbee R. E., Lipson J. and Reynolds J. H. (1956) Potassium argon dating. Geochim. et Cosmochim. Acta 10, 60-68.

Fyfe W. S., Turner F. J. and Verhoogen J. (1958) Metamorphic Reaction and Metamorphic Facies. Geol. Soc. Am. Memoir 73.

**

Gentner W., Goebel K. and Präg R. (1954) Argonbestimmungen an kalium-mineralien III Vergleichende Messungen nach der kalium-argon und uran-helium-methode. Geochim. et Cosmochim. Acta 5, 124-133.

Gentner W. and Kley W. (1957) Argon-bestimmungen an kaliummineralien - IV Die frage der argonverluste in kalifeldspaten und glimmermineralien. Geochim. et Cosmochim. Acta 12, 323-329.

Gerling E. K. (1960) Concerning the article by K. Amirkhanov, S. B. Brandt and E. N. Bartnitskii: Gerling's method of determination of activation energy of radiogenic gases in minerals. Geochemistry 7, 783-784.

Gerling E. K. Levskii L. K. and Morozova I. M. (1963) On the diffusion of radiogenic argon from minerals. Geochemistry 6, 551-555.

Gerling E. K. and Morozova I. M. (1957) Determination of activation energy of argon liberated from micas. Geochemistry 4, 359-367.

Gerling E. K. and Morozonva I. M. (1958) The kinetics of argon liberation from microcline-perthite. Geochemistry 7, 775-781.

Gerling E. K. and Morozova I. M. (1962) Determination of the activation energy for the release of argon and helium from minerals. Geochemistry 12, 1255-1268.

Gerling E. K., Morozova I. M. and Kurbatov V. V. (1960) The retentivity of radiogenic argon in ground micas. Annals N. Y. Acad. Sci. 91, Art 2, 227-234.

Gerling E. K. and Ovchinnikova G. V. (1962) Cause of low age values determined on micas by the Rb-Sr method. Geochemistry 9, 865-875.

Hart S. R. (1960) Mineral Ages and Metamorphism. Unpublished PhD thesis, M.I.T.

Hurley P. M., Hughes H., Pinson W. H. and Fairbairn H. W. (1962) Radiogenic argon and strontium diffusion parameters in biotite at low temperatures obtained from alpine fault uplift in New Zealand. Geochim. et Cosmochim. Acta 26, 67-80.

Jäger E. (1962) Rb-Sr age determination on micas and total rocks from the alps. J. Geophy. Res. 67, 5293-5306.

Jensen M. L. (1952) Solid diffusion of radioactive Na in perthite. Am. Jour. Sci. 250, 808-821.

Krogh T. E. (1964) Strontium isotopic variation and whole rock isochron studies in the Grenville Province of Ontario. Unpublished PhD thesis, M.I.T.

Kulp J. and Engles J. (1962) Discordances in K-Ar and Rb-Sr isotopic ages. Radioactive Dating, International Atomic Energy Agency, Vienna, 219-238.

Lanphere M. A. (1964) Geochronologic studies in the eastern Mojave Desert, California. J. of Geol. 72, 381-399.

Lanphere M. A., Wasserburg G. J. F., Albee A. L. and Tilton G. R. (1964) Redistribution of strontium and rubidium isotopes during metamorphism. World Beater Complex. Panamint Range, California Isotopic and Cosmic Chemistry. 269-320. North-Holland Pub. Co.

Long L. E. (1964) Rb-Sr chronology of the Carn Chuinneag intrusion, Ross-shire, Scotland. J. Geophy. Res. 69, 1589-1597.

McDougall I., Compston W. and Hawkes D. D. (1963) Leakage of radiogenic Ar and Sr from minerals in proterozoic dolerites from British Guiana. Nature 198, 564-567.

Nicolaysen L. O. (1957) Solid diffusion in radioactive minerals and the measurement of absolute age. Geochim. et Cosmochim. Acta 11, 41-59.

Nier A. O. (1938) Isotopic constitution of Sr, Ba, Bi, Tl and Hg. Phys. Rev. 54, 275-278.

Pinson W. H. (1962) A review of the preparation and calibration of shelf and spike solutions currently in use at M.I.T. in the Geochronology Laboratory. Tenth Ann. Progress Report U.S. Atomic Energy Commission Contract AT(30-1)-1381 91-97.

Pinson W. H., Fairbairn H. W. and Cormier R. F. (1958) Sr/Rb age measurements on hornblende and feldspar and the age of syenite at Chicoutimi, Quebec, Canada. Bull. Geol. Soc. Am. 69, 599-601.

Pinson W. H., Hurley P. M., Mencher E. and Fairbairn H. W. (1962) K-Ar and Rb-Sr ages of biotites from Columbia, South America. Bull. Geol. Soc. Am. 73, 907-910.

Reynolds J. H. (1957) Comparative study of argon content and argon diffusion in mica and feldspar. Geochim. et Cosmochim. Acta 12, 177-184.

Sardarov S.S. (1957) Retention of radiogenic argon in microcline. Geochemistry 3, 233-237.

Sardarov S. S. (1961) Bond energy and retention of radiogenic argon in micas. Geochemistry 1, 33-34.

Schreiner G. D. L. (1958) Comparison of the Rb^{87}-Sr^{87} ages of the Red Granite of the Bushveld Complex from measurements on the total rock and separated mineral fractions. Proc. Roy. Soc. London. Ser. A, 245, 171-178.

Shapiro L. and Brannock W. W. (1956) Rapid Analysis of Silicate Rocks. U.S.G.S. Bull. 1036-C.

Shields R. M. (1964) The Rb^{87}-Sr^{86} age of stony meteorites. Unpublished PhD thesis, M.I.T.

Sippel R. F. (1963) Na self diffusion in natural minerals. Geochim. et Cosmochim. Acta 27, 107-120.

Steyn J. G. D. (1954) Spectrographic and x-ray data on some fluorites from the Transvaal, South Africa. Min. Mag. 30, 327-332.

Tilton G. R., Wetherill G. W., Davis G. L. and Hopson C. A. (1958) Ages of minerals from the Balitmore gneiss near Baltimore, Maryland. Bull. Geol. Soc. Am. 69, 1469-1474.

Wasserberg G. J., Wen T. and Aronson J. (1964) Strontium contamination in mineral analyses Geochim. et Cosmochim. Acta 28, 407-410.

Wetherill G. W., Aldrich L. T. and Davis G. L. (1955) Ar^{40}/K^{40} ratios of feldspars and micas from the same rock. Geochim. et Cosmochim. Acta 8, 171-172.

***

Zartman R. E., Norton J. J. and Stern T. W. (1964) Ancient granitic gneiss in the Black Hills, South Dakota. Science 145, 479-481.

* Deuser, W.G. and Herzog, L.F., (1962), Rubidium-strontium age determinations on muscovites and biotites from pegmatites of the Blue Ridge and Piedmont. J. Geophys. Res., 67, 1997-2004.

** Gast, P.W. and Hanson G.N. (1963), Effects of contact metamorphism on Rb-Sr systems. Nuclear Geophysics. N.A.S.-N.R.C. Publ. 1075, 25-33.

*** Wetherill, G.W., Kouvo, O., Tilton, G.R., and Gast, P.W. (1962), Age measurements on rocks from the Finnish Precambrian, J. Geol. 70, 74-88.

APPENDIX A

TREATMENT AND DESCRIPTIONSOF MINERALS

1. Purification of the Minerals

All three biotite samples came from biotite concentrates previously prepared by various workers in the M.I.T. Geochronology Laboratory. These concentrates were first sieved into as many size fractions as possible in the -100, +300 mesh range; where grain size reduction was needed a steel pestle and mortar was used. A size fraction was then spread out on a clean piece of weighing paper and a weak hand magnet was used to remove magnetite. The grains were then passed through a Frantz Isodynamic Magnetic Separator, first at a current of approximately 0.1 amperes and then at a current of approximately 0.36 amperes. Preliminary tests showed that this range of current produced biotites of minimum impurity. The separator had a forward tilt of 25° and a side tilt of 15°. Passages were made at both of these currents until collection was entirely in one cup or the other. This procedure was repeated for every size fraction of interest and the various fractions desired were then collected in one stock bottle for subsequent use in the experiments. All samples of a particular mineral used in the hydrothermal runs came from the one stock bottle.

The Ca plagioclase came from a large hand specimen of the almost pure mineral. The main contamination proved to be magnetite and ilmenite. The mineral was crushed in a steel mortar, separated into sieve fractions, and passed through the magnetic separator at maximum current. This was repeated for every size fraction until all impurities were removed. The fractions were then collected into a large stock bottle for subsequent use.

The pegmatitic albite (cleavlandite) was treated in the same manner as described above for the Ca plagioclase. The main impurity was muscovite and this was effectively removed by magnetic treatment at the maximum current.

The fluorite contained no noticeable impurities. This was a large specimen from a vein mineral deposit. It was reduced to the desired grain size by crushing in a steel mortar and stored in a large stock bottle for subsequent use.

2. Mineral Descriptions

(a) Biotite 3086 is from the Murray Granite at Sudbury, Ontario. The colour is medium greenish brown showing slight alteration to chlorite. The main inclusions are iron oxides and a clear mineral of slightly less relief than the biotite (apatite?) This latter inclusion is seen only under the highest magnification. An estimate of the total content of inclusions is 0.5% by volume.

(b) Biotite 3205 is from the Birch Lake Granite, Hart Township, Ontario. Its colour is greenish brown showing some alteration to chlorite. Once again iron oxide and apatite(?) are the main inclusions. Estimate of inclusions is placed at 1% by volume.

(c) Biotite 3138 is from a granitic body 14 miles west of Mount Laurier, Quebec. Its colour is light brown to tan. The main inclusions are zircon with well developed pleochroic haloes, iron oxides and once again a clear mineral, probably apatite. The main inclusion is zircon. Estimate of inclusions is placed at 0.5-1.0%.

(d) The albite is of the cleavlandite variety and is from the Strickland pegmatite, Connecticut. It is part of the whole rock sample R4725 (M.I.T. laboratory collections). The mineral is free of impurities except for some alteration to sericite and kaolinite. The amount varies from grain to grain but is very minor on the whole.

(e) The calcium plagioclase, approximating to An_{50-60} in composition, is almost free of impurities except for a very slight alteration to a mineral of relatively high relief, identified as epidote. This specimen is of unknown origin. It shows good twinning but no zoning.

(f) The fluorite is very clean, and no impurities were found. It is a vein fluorite of unknown origin.

APPENDIX B

PREPARATION OF AQUEOUS SOLUTIONS

1. Solutions A and B.

Two 50 ml aliquots of a Sr^{84} enriched spike (19.5 μgms/ml) were pipetted into 100 ml vycor dishes, and evaporated to dryness. The residues were dissolved in distilled, demineralized water. One portion was transferred to a 50 ml volumetric flask, the other to a 25 ml volumetric flask. Both were taken to volume and transferred to a 50 ml (solution A) and 25 ml (solution B) polyethylene bottle for storage.

2. Solution C.

1 gram of $CaCO_3$ and 0.5 gram of $KHC_8H_4O_4$ were placed in a weighing bottle and dried overnight at 95°C. They were subsequently removed and placed in a desiccator for 15 minutes, and then weighed. The contents of the weighing bottles were placed in a 1000 ml beaker and dissolved slowly in weak (~0.1 N) HCL. The beaker was washed repeatedly with distilled demineralized water and the wash added to the volumetric flask. The flask was taken up to volume with distilled demineralized water. The contents were transferred to a 2000 ml polyethylene bottle for storage. After a temperature correction had been made, the solution was found to contain 200.02 μgms Ca/ml and 47.90 μgms K/ml at 20°C.

3. Solutions D and E.

Solution E is a previously prepared potassium standard of $KHC_8H_4O_4$ containing 1030 μgms K/ml. Solution D was prepared by pipetting 2 ml of solution E to a 50 ml volumetric flask, and taking it up to volume with distilled demineralized water. Solution D contains 41.2 μgms K/ml.

BIOGRAPHY

The author was born on July 4, 1937, in Moncton, New Brunswick, Canada, the son of Harold Ashfield and Mary Edith McNutt.

He graduated from Moncton High School in the spring of 1955 and received his B.Sc. degree, with honors, from the University of New Brunswick in the spring of 1959. He enrolled as a graduate student in the Department of Geology and Geophysics at M.I.T. in the fall of 1960.

At M.I.T., the author held teaching and research assistantships from 1961 to 1965. During the summer months of the years 1956-1961 he was engaged in geological field work in New Brunswick, northern Quebec, Saskatchewan, Alberta and British Columbia.

The author was awarded tuition scholarships from the Canadian M.I.T. Trust Fund in the years 1960-1964. He is a full member of the Society of the Sigma Xi.

The author was married on October 10, 1964 to Pauline Ann Maslack of Poultney, Vermont.