EXCESS RADIOGENIC ARGON IN PEGMATITE MINERALS

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I hereby recommend that this dissertation prepared under my
direction by A. William Laughlin

entitled EXCESS RADIOGENIC ARGON IN PEGMATITE MINERALS

be accepted as fulfilling the dissertation requirement of the
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ABSTRACT

Discordant K-Ar and Rb-Sr apparent ages were obtained on minerals from the Rutherford and Morefield pegmatites, Amelia, Virginia. Utilizing trace element data to establish a paragenetic sequence, the ages reveal a long high temperature interval following emplacement of the Rutherford pegmatite. The times of exsolution of perthite and closure of muscovite and microcline for argon loss are shown to fall on a cooling curve with $T_{\frac{1}{2}}$ equal to 30 m.y. Excess radiogenic argon is demonstrated to be present in albite, quartz, topaz and beryl. The excess argon contents of the albites apparently increased during crystallization of the pegmatite. Systematic variations in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these albites were also observed. These variations seem to have been produced by dilution of a pegmatitic melt with highly radiogenic strontium by the assimilation of wallrock containing less radiogenic strontium.

Examination of other pegmatites indicates that excess radiogenic argon is commonly but not always present in pegmatitic plagioclases. Older samples usually have incorporated larger quantities of excess argon. Recognition of both the presence of excess argon in and argon

loss from pegmatitic albites casts considerable doubt on their use as K-Ar geochronometers.

The results of diffusion experiments on natural samples indicate that approximately one third of the total argon in feldspars is rapidly lost by heating to 770°C. In microcline a value for the energy of activation of 26 kcal/mole was measured for this site. The constancy of this loss precludes heat treatments as a means of removing the excess argon.

Argon introduction experiments show that large quantities of argon may be introduced into albite at 1000°C even at argon pressures as low as one bar. The quantity introduced at one bar is approximately equal to the maximum quantity observed in nature. This introduced argon also occurs in multiple sites but the lowest energy site contains a much smaller percentage of the total argon than was observed in natural samples. A value for the energy of activation of 38 kcal/mole was measured for this site.

Additional evidence has been presented that micas in pegmatites incorporate little or no excess argon.

CHAPTER I

INTRODUCTION

In order for the potassium-argon method of geochronology to be applied to a particular mineral or rock, certain conditions and criteria must be fulfilled. These are:

- (1) The decay constants for ^{40}K must be known accurately.
- (2) The isotopic abundance of ^{40}K must be known accurately.
- (3) No ^{40}Ar must have been present at the time of crystallization of the mineral or rock.
- (4) The mineral or rock must have remained a closed system for both ^{40}K and ^{40}Ar since the time of crystallization.
- (5) The relationship between the "date" obtained and a certain geologic event must be known.

Of the five criteria listed above, the third is probably the least tested. Since any ^{40}Ar incorporated within a mineral or rock at the time of its formation will result in an anomalously old apparent age it is essential to the potassium-argon method that this criterion be thoroughly tested.

Before proceeding further a definition of terms is warranted. As recently clarified in Damon et al. (1968), radiogenic ^{40}Ar is ^{40}Ar dissolved in the reference mineral.

as a result of an external environmental ^{40}Ar pressure," Transient ^{40}Ar was defined as " ^{40}Ar produced in the reference mineral under transient conditions prior to time, $t = 0$." Inherited ^{40}Ar is " ^{40}Ar inherited from a previous set of environmental conditions prior to time, $t = 0$, excluding the transient state ^{40}Ar ." Extraneous ^{40}Ar was defined as "Any ^{40}Ar contained within a mineral separate other than the radiogenic components accumulated after a time, $t = 0$, defined by a thermal or chemical event."

In order to demonstrate the significance of extraneous ^{40}Ar as a perturbing factor in potassium-argon age determinations, Figure 1 has been prepared. This figure shows the error in the age produced by varying quantities of extraneous ^{40}Ar in minerals of differing potassium content. As would of course be expected the relative error is greatest for young minerals and for those with a low potassium content.

Prior Work

Since the potassium-argon method of geochronology achieved wide usage, there have been several investigations of the phenomena of the incorporation of excess ^{40}Ar . The most thorough of these to date have been by Damon and Kulp (1957, 1958), Livingston et al. (1967) and Damon, Laughlin and Percious (1967).

Figure 1. Errors in K-Ar Ages Produced By Extraneous ^{40}Ar

Lord Rayleigh (1933) recognized an "age effect" in the quantity of excess helium incorporated by beryls; older samples containing larger quantities. Damon and Kulp (1957, 1958) confirmed this and also recognized the "age effect" in the quantity of excess argon incorporated by beryls. They also reported large excesses in other cyclosilicates: tourmaline and cordierite. They suggested that the large quantities of excess inert gases were held in the tubular channels characteristic of these minerals. The age effect was explained as resulting from an increased rate of degassing during the early history of the earth. This increased rate due to higher heat production, would have produced higher partial pressures of the inert gases.

Livingston et al. (1967) investigated $^{40}\text{Ar}/^{40}\text{K}$ ratios in cogenetic micas and feldspars from plutonic and metamorphic environments. They observed large quantities of excess ^{40}Ar in plagioclase, plagioclase-quartz mixtures and in one orthoclase from plutonic environments. Livingston et al. reinterpreted Damon's and Kulp's (1957) data on the Beryl Mt. albite as indicating the presence of excess ^{40}Ar . They also reported concordant mica-plagioclase ages from a metamorphic terrain in southern Arizona.

Damon et al. (1967) examined the presence of excess ^{40}Ar in extrusive rocks. They observed quantities about two orders of magnitude less than in minerals from the

plutonic environment. Damon (1968) developed a mathematical treatment of the non-ideal K-Ar chronometer, reviewed the literature and further clarified the distinction between excess and inherited argon.

Hart (1961), in a study of 13 amphiboles and two pyroxenes, found no evidence for the incorporation of excess ^{40}Ar into these minerals. Later work by Hart and Dodd (1962), McDougall and Green (1964), and Lovering and Richards (1964) indicated that at least some pyroxenes from plutonic and metamorphic terrains do contain excess ^{40}Ar . Pearson et al. (1966) report an anomalous hornblende age which they think may be caused by excess ^{40}Ar . Kistler, Obradovich and Jackson (1967) reported excess ^{40}Ar in pyroxenes from the Stillwater Complex, Montana. They believe that the excess ^{40}Ar is held in one position and radiogenic ^{40}Ar in another. They conclude that it is possible to remove the excess ^{40}Ar by heating to 800°C for three hours and then obtain the true age from the ^{40}Ar remaining in the mineral. Laughlin, Damon and Watson (1968) have one hornblende sample which they believe contains excess ^{40}Ar although the evidence is not conclusive.

Several workers have observed excess ^{40}Ar in fluid inclusions in minerals. Gentner (1963) recognized it in fluorite, and Rama, Hart and Roedder (1965) demonstrated that excess ^{40}Ar could be incorporated in fluid inclusions

in quartz and fluorite. Naughton, Funkhouser and Barnes (1966) suggested that fluid inclusions were the source of the excess ^{40}Ar observed by them in biotite and olivine.

York and MacIntyre (1965) reported large excesses of ^{40}Ar in the mineral sodalite.

Method of Treatment

It is hoped that this research will illuminate two aspects of the excess argon problem: (1) the role of excess ^{40}Ar in the pegmatitic environment and (2) the presence or absence of the age effect in minerals other than the cyclosilicates. With this in mind two areas containing abundant pegmatites were studied in detail to determine the role of excess ^{40}Ar in this environment. The age effect was examined by analyzing plagioclases from several pegmatites of varying age.

In order to recognize the presence of excess ^{40}Ar in a particular mineral or rock, it is first necessary to have some independent method of evaluating the age of the sample. This age may be determined by classical stratigraphic or structural methods or by some independent isotopic geochronometer. Where possible an age obtained from some method other than the potassium-argon method is ideal. Unfortunately, age data by other methods was available for only a few of the pegmatites studied.

For the majority of the pegmatites the independent age was obtained by the potassium-argon method on cogenetic micas. The validity of these independent ages is based on several factors. Damon and Kulp (1957) were able to place maximum limits of 0.45×10^{-10} m/g on the quantity of excess ^{40}Ar incorporated in the calcium mica, margarite. Hart (1966) reduced this maximum limit to 0.031×10^{-10} m/g. The high potassium contents of the micas analyzed in this study would reduce the error produced by the observed quantities of excess ^{40}Ar to within the standard deviation of the analysis.

CHAPTER II

SAMPLE PREPARATION AND ANALYTICAL TECHNIQUES

Because many of the samples used in this study were sent to the writer by geologists working in different areas, they were often of necessity small in size. This required some modification of the usual mineral separation techniques. Larger samples were crushed in a jaw crusher and roller crusher and then reduced to an appropriate size in a pulverizer. The small samples were crushed with a steel mortar and pestle. Because most of the samples consisted largely of quartz, feldspars, and micas, good preliminary separations were obtained with an asymmetric vibrating table. Because of the flat shape of the plagioclase cleavages, it was often possible to obtain a very thorough separation of orthoclase and plagioclase using only the table. Final purifications were performed with isodynamic separators and heavy liquids.

It was critical that mineral separates of the low potassium minerals be of the highest possible purity. Separates were carefully examined under a binocular microscope during all phases of the separation and hand picking was used where necessary. The final stages in the separations were usually monitored with the low-level beta counter.

Analytical Techniques

Since a recent paper by Livingston et al. (1967) has thoroughly discussed the analytical procedures in use at the Geochronology Laboratories for the determination of potassium, rubidium, argon and strontium, only a brief description will be given here. Specialized techniques adopted for this work will be discussed in the appropriate chapters.

Potassium Analysis

Potassium analyses for most samples were performed on a modified Perkin-Elmer flame photometer using the method of Cooper (1963). Samples were digested with HF and H₂SO₄ in teflon crucibles and buffered with 1000 ppm sodium. Lithium in a concentration of 800 ppm was used as an internal standard. Because of the high rubidium concentrations in the pegmatite samples a Bausch and Lomb K768 interference filter was used on most of the potassium samples.

As reported by Damon et al. (1967), the average difference between duplicate samples in the range of 0.016-1.63% potassium is 0.52%. In the range of 2.46-19.77% potassium the average difference is 0.25%.

Accurate potassium analyses are essential particularly for the low potassium minerals since an apparent ⁴⁰Ar

excess may also be explained by a low potassium analysis. Table 1 gives the accuracy of the potassium analyses of several standard samples. Since all the standard samples contain relatively high concentrations of potassium, the U.S.G.S. standard muscovite was diluted to 0.216% potassium and analyzed. As can be seen in Table 1, the calculated and measured values are in good agreement, differing by only about 3%.

Table 1. Potassium analyses of standard samples.

Sample	Arizona Analysis %K	Comparison Analysis %K
U.S.G.S. P-207 Muscovite	8.63, 8.62, 8.68	8.58*
Bern Std. Muscovite	8.71	8.616*
U.S.G.S. P-207 Muscovite (diluted)	0.223	0.216**

*Lanphere and Dalrymple (1965).

**Mean of Arizona analyses diluted by a factor of 40.

Samples with very low potassium contents and those difficult to dissolve were analyzed for potassium by low-level beta counting. The counting techniques in use here were discussed by Damon et al. (1960). Since only the maximum potassium contents were necessary for these low

potassium minerals, corrections for beta emitters other than potassium were not made.

Argon Analysis

The argon analyses were made on a Nier, 6 inch 60° mass spectrometer operated dynamically. Fusion, and in the case of the diffusion experiments, heating, was accomplished by a Westinghouse R.F. generator. During fusion a high purity ^{38}Ar isotopic diluent was admitted by spike ampoule. The gases released were purified with a Grandt style titanium furnace, copper oxide furnace, and artificial zeolites. All samples were checked for the presence of hydrogen before being admitted into the mass spectrometer. The absence of any hydrogen was essential to prevent the formation of $^1\text{H}^{35}\text{Cl}$ which is not resolvable from ^{36}Ar .

Precision of the argon analyses in this work is shown in Table 2. Duplicate analyses of four samples yield an average difference of 0.97%. Table 3 gives the accuracy of the analyses as reflected in the results of the analysis of interlaboratory standards.

X-Ray Fluorescence Analysis

The x-ray fluorescent method was used for the determination of rubidium and strontium for trace element studies and, in conjunction with isotopic dilution determinations of rubidium and strontium, for the dating of

Table 2. Precision of four duplicate argon analyses.

Sample Number and Mineral	$^{40}\text{Ar} \times 10^{-10}$ m/g	^{40}Ar atmos. %	Difference %
AWL-5-65m, muscovite	42.34 41.50	41.5 5.4	1.00
AWL-23-66, muscovite	15.00 15.37	6.0 2.6	1.22
AWL-20-66t, tourmaline	7.175 7.094	10.6 6.6	0.57
AWL-15-66, spodumene	20.19 19.75	1.1 14.1	1.10
			Av. 0.97

Table 3. Argon analyses of standard samples.

Sample	Arizona Analysis $^{40}\text{Ar} \times 10^{-10}$ m/g	Comparison Analysis $^{40}\text{Ar} \times 10^{-10}$ m/g
U.S.G.S. P-207	12.75, 12.73, 12.62	12.67*
Bern Std. Muscovite	2.794, 2.724, 2.732	2.863** 2.76***

*Av. of 10 labs. Lanphere and Dalrymple (1965).

**Av. of two determinations by U.S.G.S. Lanphere and Dalrymple (1965).

***Steiger (1964).

samples from the Amelia, Virginia pegmatites. The method as used at the Geochronology Laboratories, University of Arizona, has been described in the annual progress reports of the laboratory to the AEC (Damon et al., 1965, 1966, 1967).

Determinations were made on a Norelco x-ray unit using a molybdenum target and a LiF analyzing crystal. Data reduction was by a modification of the method of Reynolds (1963). Samples were prepared by grinding to -200 mesh in a Pitchford blender and pressing into bakelite supported briquettes.

Except in the case of samples with very high concentrations of rubidium and/or strontium or with unusual compositions, the x-ray fluorescent method gives results comparable to those obtained by isotope dilution. Considerable difficulty was encountered in the analysis of microcline and zinnwaldite from the Amelia pegmatites. The rubidium contents of these samples were exceedingly high and as may be seen in Table 4 the initial x-ray fluorescent results were in poor agreement with isotope dilution. To reduce the rubidium concentrations, the powdered samples were mixed with rubidium free Ottawa sand in ratios of 13-18 parts sand to one part sample and re-ground. Analysis of briquettes prepared from the mixtures gave good agreement with the isotope dilution results. The

Table 4. Isotope dilution and x-ray fluorescence results for samples from Amelia, Virginia.

Sample Number	Mineral	X-ray	Undiluted	X-ray	Diluted	Isotope	Dilution
		Rb ppm	Sr ppm	Rb ppm	Sr ppm	Rb ppm	Sr ppm
AWL-22-65a	Albite	101.5	13.3	--	--	96.64	17.36
AWL-22-65m	Microcline	2891.6	11.8	2443.4	--	2587.1	16.76
						2467.1	17.14
AWL-22-65w.r.	Perthite	2635.7	13.9	2313.4	--	--	--
AWL-23-65	Zinnwaldite	9203.2	5.59	8471.5	--	8333.8	12.38

original results may have been in error because of the high rubidium concentrations and/or enhancement of rubidium by another element.

Rubidium-Strontium Mass Spectrometric Analysis

The mass spectrometric rubidium-strontium determinations were made on a six-inch, 60° mass spectrometer. Rhenium filaments were used in a triple filament configuration. Measurements were made using the expanded scale method and employing beam switching.

The samples were digested in teflon crucibles using hydrofluoric acid. After solution the samples were dried and then taken up in hydrochloric acid and placed on ion exchange columns. The samples were loaded on the rhenium filaments after separation of the rubidium and strontium.

In general at least three runs were made on each sample. Each run consisted of two backgrounds of the m/e range of interest and at least 12 sets of peaks. The peak heights were then measured, followed by data reduction using an Olivetti Programma computer.

CHAPTER III

PEGMATITES OF THE AMELIA DISTRICT, VIRGINIA

The pegmatites of the Amelia district of Virginia are typical of the many pegmatites found in the Appalachian Piedmont. Although numerous workers have written on the individual minerals found in these pegmatites, little has been written on the geologic setting of the pegmatites themselves. The most thorough discussion of the geology of the district is found in U. S. Geological Survey Prof. Paper 248 (Lemke, Jahns and Griffitts, 1953). Much of the following description is taken from that publication.

Location and Geologic Setting

The Amelia district lies in the Virginia Piedmont about 40 miles southwest of Richmond (Figure 2). It is a large area, roughly four miles wide by ten miles long, containing at least 83 mines and prospects. The host rock of the pegmatites is the Wissahickon granitized gneiss which consists of quartz-biotite schists, biotite augen gneisses, garnet-mica schists and gneisses, and hornblende schists and gneisses. In places Lemke et al. (1953) recognized bedding and conglomeratic layers indicating a sedimentary origin for at least part of the sequence.

Figure 2 Location Map, Rutherford and Morefield Pegmatites, Amelia, Virginia

The major igneous rock in the district is the Red-oak granite which occurs south of Amelia as northward trending prongs. The Redoak granite, in reality a fine to medium grained biotite quartz-monzonite, is strongly foliated and contains partially digested inclusions of schist and gneiss. Lemke et al. believe that this rock may be the source of the pegmatites.

The Amelia district may be subdivided into two smaller regions: the Jefferson-Amelia area and the Morefield-Denaro area. Although the pegmatites in the two areas are similar, certain differences do exist, the most important of these being the continuity of the pegmatites. In the Morefield-Denaro area the pegmatites are longer and more continuous and show less tendency to pinch out with depth. In both areas the pegmatites are discordant with minor apophyses complicating the structure. The pegmatites in both areas are commonly well zoned and contain cores of massive quartz.

Although numerous simple pegmatites occur in the Amelia district, the two pegmatites furnishing the samples used in this study, the Rutherford and the Morefield, are characterized by many of the rarer pegmatite minerals, are zoned, and must be classified as complex pegmatites.

Rutherford Pegmatite

The Rutherford pegmatite which lies in the Jefferson-Amelia area is a large, irregularly zoned, discontinuous pegmatite. It is generally discordant with minor concordant and discordant branches. In most places it is less than 10 feet thick. Zoning consists of a quartz core, an intermediate zone of coarse, blocky perthite, a plagioclase rich wall zone and a border zone of muscovite, biotite, quartz and plagioclase. The biotite in this border zone probably results from reaction with the wall rock. Two kinds of albite occur in the pegmatite: moonstone, a chatoyant white variety, and clevelandite, a clear tabular variety.

The mineralogical composition of the zones generally follows Bowen's reaction series, and Lemke et al. (1953) believed that the pegmatite crystallized from the walls inward. The origin of the clevelandite presents the major problem in the crystallization of the pegmatite. Lemke et al. considered that much of it formed at the expense of earlier crystallized quartz and feldspar and that its replacement was controlled by fractures. This clevelandite is the host mineral for most of the rarer minerals which crystallized in its interstices.

Morefield Pegmatite

The Morefield pegmatite which lies in the Morefield-Denaro area is also a complexly zoned pegmatite. It trends N45°E and dips steeply to the northwest. It is a large pegmatite, 1100 feet long and 5-30 feet thick, and is sharply discordant.

The zoning is roughly the same as in the Rutherford pegmatite. The core consists chiefly of smoky quartz with some perthitic microcline crystals while the intermediate zone is largely coarse perthite with minor albite, quartz and mica. The contact between the core and intermediate zone may be marked by large crystals of beryl, topaz, phenacite and mica. The wall zone is made up of medium to coarse grained plagioclase, quartz, mica and perthite. As at the Rutherford mine the border zone is rich in biotite with fine grained quartz and spessartite.

The genesis of the Morefield pegmatite is probably similar to that of the Rutherford. Crystallization from the walls inward was the dominant process with perhaps some minor late stage replacement. Lithium and fluorine appear to have been abundant in this pegmatite since zinnwaldite and topaz occur as late stage minerals.

Numerous criteria point to a magmatic origin for these two pegmatites. Both have fine-grained border zones showing some reaction with the wall rocks. Both generally

follow Bowen's reaction series with the exception of some clevelandite which may be of replacement origin. The abundance of the rare minerals, especially those containing the volatile elements, suggests a magmatic origin. Although the source of the magma is not known, little doubt exists that the pegmatites crystallized from a magma.

Prior Geochronological Work

Little work has been done on the geochronology of the pegmatites of the Amelia district. Prior to this study Rb-Sr measurements had been made on muscovites from three pegmatites from the district, and isotopic lead determinations had been made on two samples of potassium feldspar. Some additional evidence is available from regional geologic and geochronological studies in the Appalachians. Much of this evidence is subjective, however, and open to interpretation.

The pegmatites of the Amelia district, as has been discussed above, intrude the Wissahickon schists and gneisses which were believed by Lemke et al. (1953) to be Precambrian in age. The Wissahickon schist is part of the Glenarm series which overlies the Baltimore gneiss. Intensive studies of the age relationships of the Glenarm series by Steiger and Hopson (1964), Hopson (1964) and Wetherill et al. (1966) strongly suggest that the Wissahickon

schist is older than 550 ± 50 m.y. These studies place probable older limits on the Amelia pegmatites of about 550 m.y.

Deuser and Herzog (1962) analyzed a series of micas from the Blue Ridge and Piedmont regions by the Rb-Sr method. They found that the Blue Ridge pegmatites ranged in age from 225 m.y. to 550 m.y. with a mean of 316 m.y. excluding the two high dates. The Piedmont dates ranged from 255 m.y. to 330 m.y. with a mean of 287 m.y. They recognized that these dates could represent either discrete events or differential response to metamorphism. Three of their samples were muscovites from the Amelia district which gave an average age of 273 m.y. This suggested to them that the 250 m.y. event recognized in the southern Blue Ridge and Piedmont might extend as far north as Amelia.

Potassium-argon ages of micas from the Blue Ridge and Piedmont regions obtained by Kulp and Eckelmann (1961) indicated a polymetamorphic history for the area. They recognized several metamorphic belts trending northeast and concluded that the initial metamorphism occurred at least 1100 m.y. ago and that later events probably took place at 850 m.y., 550-450 m.y., 350 m.y. and 250 m.y. Evidence was presented that each of the successive events occurred in a belt of decreasing width. It appears that the Amelia district lies near the boundary of the 350 m.y.

and the 250 m.y. belts. The numerous pegmatites could have been emplaced at either of these times or possibly emplaced earlier and metamorphosed at 350 m.y. or 250 m.y. No textural or mineralogical evidence exists for such a metamorphism of the pegmatites, however.

Two lead analyses on potassium feldspars from the area offer little additional evidence on the age of the pegmatites. A summary of the lead data is presented in Table 5. Catanzaro and Gast (1961) reported a model age of 200 ± 200 m.y. and compared this with an accepted age of 350 m.y. Although they do not give the source of their accepted age, it may be from analogy with the Spruce Pine pegmatites which yield many 350 m.y. ages. As shown in Table 5 the lead data, using several different models, give ages ranging from 239 m.y. to 394 m.y.

In summary, although the geochronological data are meagre and inconclusive, they do suggest that the pegmatites of the Amelia district were emplaced less than 400 m.y. ago and most probably about 273 m.y. ago.

Analytical Results

Potassium-Argon Analyses

Potassium and argon analyses were run on seven different mineral species from the Amelia district. The minerals analyzed may be divided into two groups: those with

Table 5. Prior geochronological work on pegmatites, Amelia, Virginia.

Lead Data					
Mineral	Location	207/204	207/204	208/204	Reference
K-feldspar	Morefield pegmatite	18.18	15.67	38.41	Catanzaro and Gast (1961)
K-feldspar	Amelia, Va.	18.20	15.70	38.29	Doe, Tilton and Hopson (1965)
Lead Model Ages*					
Model	H.H.	R.S.F.		R.F.C.	
		206/207	208/204	206/204	208/204
Age m.y.	376	276	239	351	394
Rb-Sr Data					
Mineral	Location	Apparent Age m.y.		Reference	
Muscovite	Morefield peg.	261		Deuser and Herzog (1962)	
Muscovite	Champion peg.	270		" " " "	
Muscovite	Rutherford peg.	289		" " " "	

*H.H.--Holmes-Houtermans Model

R.S.F.--Russell, Stanton and Farquhar Model

R.F.C.--Russell, Farquhar and Cumming Model

a high potassium content, commonly used for K-Ar dating, and those with low potassium contents which might be most expected to show any excess ^{40}Ar present. The first group would include muscovite, zinnwaldite, microcline, and perhaps albite. Although albite does not have a high potassium content and has been rarely used for K-Ar dating, plagioclases more calcic than these have been widely used. The second group includes topaz, quartz and beryl, the last two of which have been previously demonstrated to contain excess ^{40}Ar (Damon and Kulp, 1958; Rama et al., 1965).

To obtain the "best" K-Ar age on these pegmatites two samples of muscovite and one of zinnwaldite (a fluorine-rich mica) were analyzed. The results of these analyses are shown in Table 6. The mean mica age is 248 ± 4 m.y. Since micas are of course sensitive to any thermal perturbation this age may represent either the initial time of cooling following original crystallization, the time of latest metamorphism if such occurred, or some intermediate time. To distinguish between excess and inherited ^{40}Ar it is important to determine which event is represented by the 248 m.y. date.

Three samples of the green amazonstone variety of microcline were also analyzed. All of this microcline was in reality a microcline perthite with albite present as stringers and exsolution lamellae. One of the samples

Table 6. Potassium argon analyses, Amelia, Virginia.

Sample Number	Mineral	Pegmatite	K %	^{40}Ar $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %	Apparent Age	Apparent** Excess ^{40}Ar $\times 10^{-10}\text{m/g}$	Apparent*** Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
AWL-5-65m	Muscovite	Rutherford	8.69 $\pm$ 0.05	42.34 41.50	41.5 5.4	256 $\pm$ 8 251 $\pm$ 8	-- --	
AWL-18-65	Muscovite	Rutherford	8.63 $\pm$ 0.05	40.07	6.6	245 $\pm$ 7	--	
AWL-23-65	Zinnwaldite	Morefield	8.30 $\pm$ 0.06 8.29 $\pm$ 0.01	38.37	15.2	244 $\pm$ 7	--	
AWL-12-65	Microcline	Rutherford	11.80 $\pm$ 0.05 11.82 $\pm$ 0.04	47.41	2.4	213 $\pm$ 6	--	
AWL-22-65w.r.	Perthite	Rutherford	10.87 $\pm$ 0.03 10.88 $\pm$ 0.02	47.20	1.5	230 $\pm$ 7	--	
AWL-22-65m	Microcline	Rutherford	11.80 $\pm$ 0.03 11.77 $\pm$ 0.02	51.46	2.1	231 $\pm$ 7	--	
AWL-22-65a	Albite	Rutherford	0.406 $\pm$ 0.004 0.406 $\pm$ 0.001	3.621	7.9	445 $\pm$ 13	1.710	1.348
AWL-5-65a	Albite	Rutherford	0.14 $\pm$ 0.0004 0.14 $\pm$ 0.0014	1.065	39.8	384 $\pm$ 15	0.406	0.281
AWL-19-65	Albite	Morefield	0.16 $\pm$ 0.02 0.16 $\pm$ 0.02	1.323	64.6	416 $\pm$ 21	0.570	0.493****
AWL-24-65	Albite	Rutherford	0.23 $\pm$ 0.0006 0.23 $\pm$ 0.0004	1.582	23.3	352 $\pm$ 11	0.499	0.294
AWL-25-65	Albite	Rutherford	0.19 $\pm$ 0.001 0.19 $\pm$ 0.002	1.097	25.4	297 $\pm$ 9	0.192	
AWL-13-65	Albite	Rutherford	0.110 $\pm$ 0.006 0.114 $\pm$ 0.011	0.6071	57.2	283 $\pm$ 11	0.079	
AWL-21-65	Beryl	Rutherford	0.01 $\pm$ 0.001 $\pm$ 0.009 $\pm$ 0.001	186.2	15.8 (Leak)		186.0	
AWL-30-65	Quartz	Rutherford	$\approx$ 0.03*	0.988	31.0		$\approx$ 0.847	$\approx$.820
AWL-26-65	Topaz	Morefield	$\approx$ 0.06*	1.271	60.0		$\approx$ 1.00	$\approx$.935

*Low level beta counting.

**Based on 248 m.y.

***Based on 292 m.y.

****Based on 272 m.y.

(AWL-22-65w.r.) was analyzed as a "whole rock" perthite. This sample was prepared by removing the outer surface of the perthite and crushing the fresh inner material. The sample was split without sieving and total splits were used for the potassium and argon analyses. This treatment prevented any loss of the albite fraction in the finer material. After splits were taken for analysis, the remainder of the sample was crushed to -80+150 mesh and the albite and microcline were carefully separated with heavy liquids. As can be seen by examining the results of the potassium analyses for the albite (AWL-22-65a) and the microcline (AWL-22-65m) very pure separates were obtained. The third microcline (AWL-12-65) was a different sample, having been crushed to -20+48 mesh and purified with heavy liquids. Some of the albite fraction was removed during this separation.

All of the microclines yielded ages distinctly younger than the mean mica age of 248 m.y. The "whole rock" perthite and the microcline separated from it show a loss of about 8% of their radiogenic ^{40}Ar while AWL-12-65 shows a loss of 14% with respect to the 248 m.y. age. This loss of radiogenic ^{40}Ar from potassium feldspars is in accord with results obtained by other workers (Wetherill, Aldrich and Davis, 1955; Carr et al., 1956; Folinsbée et al.,

1956; Wasserburg, Pettijohn and Lipson, 1956; Goldich et al., 1961; Wetherill et al., 1966).

Six samples of albite were analyzed. In addition to the albite separated from the perthite, two samples of the chatoyant moonstone variety, two of clevelandite and one of blocky blue albite crystals were run. As may be seen in Table 5 all six samples gave ages greater than 248 m.y.

An isochron plot (Figure 3) of the K-Ar results clarifies the differences between the mica, microcline and albite data. A 248 m.y. isochron was constructed based on the mean mica age. The six albite samples plot above this line while the three microclines plot below the line. Since the low microcline apparent ages agree with the results obtained by other workers on potassium feldspars little further discussion of these results is warranted. It is interesting to note, however, that the Amelia microclines have lost only 8-14% of their radiogenic ^{40}Ar , relative to the mean mica age, somewhat less than most other potassium feldspars measured.

In an attempt to resolve the anomalous results from these pegmatites, minerals with very low potassium contents were next analyzed. The most ubiquitous mineral with a low potassium content is quartz. A sample of quartz from the Rutherford pegmatite was crushed to -48+65 mesh and

the potassium content was determined by low-level beta counting. No beta activity above background was detected. The error on this measurement would indicate that the potassium content is less than 0.03%. The quartz was heated in two stages (see Chapter VI) with a total of 0.988×10^{-10} m/g of ^{40}Ar being removed. Since no potassium was detected in this sample, essentially all of the ^{40}Ar must have been incorporated at the time of crystallization or introduced at some later time, i.e., it could not have formed in situ and must therefore be excess.

The second low potassium mineral analyzed was topaz. Low-level beta counting indicated a maximum potassium content of 0.06%. Because of the presence of fluid inclusions this sample was also heated in several steps. Only the total ^{40}Ar released is of interest at this point, however. Although complete fusion was not attained, 1.271×10^{-10} m/g of ^{40}Ar were released. Of this quantity 78.7% would be extraneous with respect to the mica age.

One additional low potassium mineral was analyzed. This was a sample of beryl from the Rutherford pegmatite which had a potassium content of 0.01%. Since Damon and Kulp (1958) had previously demonstrated that beryls contain large quantities of excess ^{40}Ar this sample was run primarily to allow comparison with their results. Analysis of

the Amelia beryl indicated an excess of 186×10^{-10} m/g of ^{40}Ar .

Summary of Potassium-Argon Results. Although the beryl, quartz and topaz clearly contain excess ^{40}Ar the albites can not as yet be demonstrated to do so. It is obvious that with respect to the mean mica age they contain extraneous ^{40}Ar but without knowing the significance of the 248 m.y. age it is impossible to say whether this is excess or inherited ^{40}Ar . In an attempt to determine the meaning of this date, trace element and Rb-Sr studies were made on the two pegmatites.

Trace Elements Analyses

Since excess ^{40}Ar is simply a gaseous trace element, its concentration in a mineral should reflect the argon partial pressure in the melt at the time of crystallization and the solubility of argon in the mineral. If the order of crystallization is known for a series of minerals then it might be possible to evaluate pressure changes in the melt during crystallization by measuring the excess ^{40}Ar contents of the minerals. The five albite samples from the Rutherford pegmatite which apparently contained widely varying excess ^{40}Ar contents offered an excellent opportunity to test this idea. Unfortunately, the Rutherford pegmatite has been almost completely mined out and all of the samples came from the mine dumps. It was thus impossible to determine

the order of crystallization of the samples analyzed from structural or textural evidence.

In an attempt to determine the order of crystallization of the five albites, the behavior of potassium, rubidium, and strontium in the feldspars was examined. It was also hoped that the trace element data would shed some light on the origin of the microcline perthite and place some limits on the temperature range of crystallization of the pegmatite.

The most likely index of differentiation and thus of the order of crystallization is the K/Rb ratio. This ratio has been widely used as an index of differentiation since rubidium is enriched in the later differentiates of a magma. Heier and Taylor (1959) and Hahn-Weinheimer and Ackerman (1967) for example show decreases in K/Rb ratios toward the center of granite intrusions. Rubidium is a ubiquitous trace element, commonly substituting for potassium. Its electronegativity and ionization potential are about the same as potassium but it is slightly larger in size (Table 7). The increased size of the Rb^+ only allows admission into the K^+ site and the Rb^+ is thus concentrated in the later fractions of the crystallizing melt. Rubidium forms no minerals of its own but is commonly enriched in pollucite, micas and feldspars from pegmatites. Taylor (1965) gives the crustal abundance of rubidium as 90 ppm

and the average crustal K/Rb ratio as about 230. He also states that to produce a K/Rb ratio of less than 100, "a large scale fractionation process is necessary."

Table 7. Ionic radius, electronegativity, ionization potential and bond energy of Na^+ , K^+ , Rb^+ and Sr^{2+} .

	Radius*	Electro- negativity*	X-O Bond Energy** kcal/mole	Ionization Potential*** V
	A			
Na^+	0.95	0.9	117	5.14
K^+	1.33	0.8	105	4.34
Rb^+	1.48	0.8	99	4.2
Sr^{2+}	1.13	1.0	223	11.03

*Fyfe (1964)

**Damon (1968)

***Ahrens (1964)

The behavior of rubidium in the pegmatitic environment is extremely interesting. Since pegmatites are highly differentiated rocks they are in general enriched in the alkali metals excepting sodium (Heier and Adams, 1964). Simple pegmatites, even if of large size, are usually not enriched in rubidium and show K/Rb ratios near the crustal average. Complex pegmatites may show considerable enrichment in rubidium and thus low K/Rb ratios.

The potassium, rubidium and strontium contents were determined for a suite of minerals from the Amelia pegmatites. The analytical data and the resulting ratios are given in Table 8 and Figure 4. The mineral showing the greatest rubidium enrichment was zinnwaldite with a K/Rb ratio of 9.8. Two effects have operated to yield a low ratio in this mineral. Zinnwaldite is a very late mineral in the Morefield pegmatite and would thus be expected to show considerable enrichment of rubidium. This value is also in accord with Taylor's statement that rubidium enters the mica structure more easily than the feldspar structure (Taylor, 1965). The five samples of albite from the Rutherford pegmatite show an extreme range in ratios varying from 243.5 to 40.0. This large variation in ratios is indicative of extreme fractionation within the pegmatite. According to Taylor's ideas the large variations in ratio, and the low values of the ratio for three of the albites, would suggest a source from a residual granitic magma. This conclusion may not be completely warranted, however. Once a pegmatitic magma has been formed, either as a product of differentiation of primary granitic magma or as a product of partial anatexis, the same thermodynamic laws will be obeyed by the system. Extreme fractionation of K and Rb cannot be used to unequivocally distinguish between all sources of the magma. In addition, the low K/Rb ratios do

Table 8. Trace element contents of minerals from Amelia, Virginia.

Sample Number	Mineral	K %	Rb ppm	Sr ppm	K/Rb	Rb/Sr	Excess ^{40}Ar x 10^{-10}m/g	(87/86) ₀
AWL-22-65w.r.	Perthite	10.88	2313.4	13.9	47.0	166.4		
AWL-22-65m	Microcline	11.79	2443.4	12.8	48.3	190.9		
AWL-22-65a	Albite	0.406	93.6	11.9	40.0	7.86	1.710	
AWL-24-65	Albite	0.23	27.6	49.7	61.6	0.555	0.499	0.7335
AWL-25-65	Albite	0.19	13.7	38.5	138.7	0.356	0.192	0.7392
AWL-5-65a	Albite	0.14	5.89	16.6	237.3	0.355	0.406	0.7543
AWL-13-65	Albite	0.112	4.60	28.6	243.5	0.161	0.079	0.7414
AWL-22-65	Zinnwaldite	8.30	8471.5	12.4	9.80	683.2

Figure 4. K vs. Rb in Minerals
from the Rutherford and Landsverk Pegmatites

not necessarily indicate a granite differentiate source. Granites, shales and graywackes all have very similar rubidium contents in the range from 120 to 150 ppm (Taylor, 1965). If the shales or graywackes were either partially or completely melted, the rubidium content of the resulting melt would either equal or exceed the rubidium content of the average granite. Partial melting could result in a rubidium enriched melt since the early melting feldspars contain the bulk of the rubidium (Taylor, 1965). If such a melt, having the same rubidium content as a granite, is formed, similar fractionation processes could then act, yielding low K/Rb ratios. Although it is believed that the rubidium concentrations and the K/Rb ratios cannot be used to unequivocally identify the ultimate source of the pegmatitic magma, these data may give some indication of the order of crystallization of the albites. Taylor (1965) has stated, "Increases in rubidium relative to potassium in a sequence of granites or within a pegmatite can be interpreted as indicating the order of intrusion."

The Amelia, Virginia albites are high sodium albites. The average of nine analyses of Amelia samples given by Deer, Howie and Zussman (1963) indicates a composition of $Ab_{96.9} \pm 1.9$, $An_{1.3} \pm 1.2$, $Or_{1.8} \pm 1.0$. The potassium contents of the five albites were uniformly low with a maximum of 0.406% potassium in the albite separated from the perthite. The higher potassium content of this sample may represent an

incomplete separation of microcline. The sample was repeatedly floated with heavy liquids, however, and it is believed that the microcline contamination, if any, was extremely low. If the albites are ordered by their increasing potassium contents it can be seen that the rubidium contents vary similarly. In the same order the K/Rb ratios decrease along a straight line on a log-log plot from near the average crustal ratio of 230 to 40. This decrease reflects fractionation within the Rutherford pegmatite and should indicate the order of crystallization of the albites.

It is interesting at this point to note that Taylor, Heier and Sverdrup (1960) show a log-log plot of the K/Rb ratios of five albites and their cogenetic potassium feldspars from a Norwegian pegmatite. These five albites present a linear array with approximately the same slope and intercept as the line for the Rutherford albites. These data have been replotted on Figure 4 to allow ready comparison with the Amelia data. Taylor et al. (1960) believe that these albites represent three generations of crystallization and that generations I and II show a relationship in trace element content. They believe that the generation II potassium feldspars resulted from the metasomatic alteration of generation I potassium feldspars. The generation III potassium feldspars were present as coatings and in cracks in the earlier feldspars.

In high sodium albites both potassium and rubidium may be regarded as trace elements. The observed pattern of their behavior can be readily explained by consideration of the X-O bond energies (Damon, 1968). The X-O bond energies for Na^+-O , K^+-O , Rb^+-O and $\text{Sr}^{+2}-\text{O}$ are 117, 105, 99, and 223 kcal/mole respectively. In the albites, the K^+ and Rb^+ substitute for Na^+ , a slight preference being shown for K^+ over Rb^+ . It is to be expected then, that in a series of albites, the later ones to crystallize should be enriched in both potassium and rubidium. The preference for K^+ over Rb^+ would lead of course to decreasing K/Rb ratios as crystallization proceeds.

The behavior of the Sr^{+2} is somewhat more complex. Strontium commonly substitutes for Ca^{+2} and because of its lower X-O bond energy, 223 kcal/mole vs. 236 for $\text{Ca}^{+2}-\text{O}$, it would be expected to be enriched in the later calcium minerals. Strontium may also substitute for K^+ and Na^+ , however, and in this case it would be expected to be captured by the earlier potassium and sodium minerals. Since calcium concentrations are low in the Amelia albites, it seems likely that the Rb/Sr ratios would increase during crystallization. This is found to be the case.

Although the order of crystallization of the samples analyzed could not be determined from structural or textural evidence, Lemke et al. (1953) concluded that the microcline perthite crystallized after the moonstone variety of albite

Figure 5. General Paragenetic Sequence for Feldspars in Pegmatites of the Southeastern Piedmont. Modified from Lemke et al. (1953)

(Figure 5). Some of the clevelandite was believed to be the latest albite. The K/Rb ratios, the Rb-Sr ratios and the increasing potassium and rubidium contents agree in placing the crystallization of the perthite after the moonstone but they indicate that the clevelandites were the first to crystallize among the albites analyzed. This conclusion does not necessarily hold for clevelandites from other pegmatites or even for all clevelandites from the Rutherford pegmatite.

There is another possible interpretation of the clevelandites having potassium and rubidium contents lower than the other albites. If the clevelandites had indeed crystallized after the microcline, it is possible that the large quantity of crystallizing microcline would have depleted the melt in potassium and rubidium producing lower concentrations of these elements in the clevelandite. This work and that of Taylor et al. (1960) indicate that there is essentially no difference in K/Rb ratios between cogenetic potassium feldspar and albite. Since this is the case, any albite crystallizing after the microcline could have lower potassium and rubidium contents but the K/Rb ratio would still have to be less than 40. Thus any albite later than the microcline must plot to the right of the 45° line through the microcline-albite pair.

The Norwegian albites lie on the same line as do the Amelia albites but the generation III samples appear to be out of sequence. These two samples have higher K/Rb ratios

than do samples from generations I and II which are in the expected order. The cause of this anomalous behavior is uncertain.

Let us now consider the significance of the albites lying on a straight line on a log-log plot. The equation of this line is $\log \text{Rb}(\text{ppm}) = 2.929 + 2.433 \log \text{K}(\%)$. In a recent abstract, Shaw (1967) reported the equation $\log \text{Rb}(\text{ppm}) = 1.597 + 1.115 \log \text{K}(\%)$ as explaining the relationship between potassium and rubidium in 12 igneous rock suites. These suites were not pegmatites, however, so a direct comparison between the equations is not possible. Comparison of the slopes of the two lines does show that fractionation of the melt was more extreme in the Rutherford pegmatite. The slope of the line for the 12 igneous rock suites is 42° , indicating only a slight preference for potassium over rubidium. The pegmatite line has a slope of 22° , showing a high enrichment of rubidium in the albites.

McIntire (1963) has recently discussed the conditions necessary for a logarithmic distribution of a trace element of crystals growing from a solution or melt. In brief, such a distribution is produced by a lack of equilibrium between the growing crystals and the melt or solution. This failure to equilibrate could be caused by removal in the crystals from contact with the solution or melt, slow diffusion of the trace elements in the crystals, or the incomplete mixing of the solution or melt.

A zoned pegmatite should furnish an ideal example of a rock body in which the minerals have failed to maintain equilibrium with the melt. The zoning itself is indicative of the failure to equilibrate while the common observation that more calcic plagioclases are found in the border and wall zones and the more sodic plagioclases are located in the intermediate zones and the core indicates that equilibrium was not maintained between the zones during crystallization. Thus we may expect a zoned pegmatite to show a logarithmic distribution of trace elements.

Origin of perthite. The results of the potassium, rubidium, and strontium analyses of the perthite, and the albite and microcline separated from it, are of additional interest since they lend support to textural evidence on the origin of the perthite. As Gates points out in Emmons (1953) three theories are generally accepted for the formation of perthites. These are: unmixing, simultaneous crystallization, and replacement. Each of these theories may be tested in the light of the trace element data.

This particular perthite from the Rutherford pegmatite is the green amazonstone variety and is very coarse grained. Heating experiments indicate that the green color is permanently lost at temperatures between 350°C and 375°C while heating to lower temperatures (about 200°C) produces a brown color which changes back to green on cooling. The

albite is present in two forms, exsolution lamellae, and veinlets up to 2 mm in width. The lamellae of albite are generally absent near the veinlets suggesting that the veinlets were formed by the draining of the lamellae.

Since the potassium contents of the microcline and perthite are known it is possible to estimate the quantity of the Ab molecule in them both. The Or content of the perthite is 80%, leaving 20% for the sum of Ab and An. The microcline separated from the perthite has an Or content of about 87%. Since the An content is generally low, as shown by Deer et al. (1963), it may be neglected. The difference in Ab contents between the microcline and the perthite is 7%, which must be present as a separate phase. Petrographic examination and mass balance calculations based on the potassium and argon contents indicate an Ab content of 8-9%, present as a separate phase in the perthite.

Since the textural evidence in the perthite suggests an origin by exsolution or unmixing, this theory will be first compared with the trace element data. Exsolution in a microcline perthite may be thought of as the diffusion of Na^+ into a certain area and the accompanying diffusion of K^+ out of that area. During these changes the overall structure should remain nearly the same. The Rb^+ is originally present in the perthite substituting for the K^+ . As the K^+ is removed and Na^+ substituted for it to form albite,

the K/Rb ratio will be governed by the diffusion coefficients of the two ions, K^+ and Rb^+ . These coefficients will in part be dependent upon the total bond energy of the X-O bonds. Because of the close similarities of these values for K^+-O and Rb^+-O and because of the similar radii, it would be expected that K^+ and Rb^+ would behave in a similar fashion. Thus, the K/Rb ratio should remain approximately the same in the two phases. Strontium, however, with its much higher bond energy would be more tightly bound and its concentration should remain relatively constant during the exsolution process.

Let us now consider the possibility that the perthite was formed by simultaneous crystallization of microcline and albite. Taylor et al. (1960) examined the K/Rb ratios in K-feldspars and plagioclase that crystallized at the same time and found that they were essentially the same. The results obtained on the Amelia samples would thus be in accord with this theory. The behavior of the Sr^{+2} would again be more complex. As discussed above, Sr^{+2} may substitute for Ca^{+2} , Na^+ or K^+ . The calcium contents of the albite and microcline probably do not vary significantly so that there are probably roughly equal contributions to the total strontium concentrations from the substitution of Sr^{+2} for Ca^{+2} . The capturing of Sr^{+2} by K^+ and Na^+ leads to roughly equal strontium concentrations in the microcline

and albite. It is evident that the trace element data does not eliminate an origin of simultaneous crystallization.

The third theory of perthite formation has many proponents. It is generally thought that late sodium-rich solutions have reacted with a potassium feldspar, especially along cracks, to form albite. This theory is difficult to reconcile with the trace element data on the Rutherford perthite. The late replacing or reacting solution should have a lower K/Rb ratio than the solution or melt from which the microcline crystallized. It is hard to visualize a process whereby such a solution could react with microcline along fractures to produce albite with the same K/Rb ratio as the host microcline. A reaction of this type would be expected to produce albite with a lower K/Rb ratio than that of the microcline.

The sequence of albites with increasing potassium contents followed by a perthite with an Or content of 80% gives some indication of the conditions under which the pegmatite must have crystallized. If the phase diagrams of the system albite-orthoclase (Bowen and Tuttle, 1950; Yoder, Stewart and Smith, 1957) are examined it is readily seen that at water pressures of less than 2000 bars the first potassium feldspar to crystallize after albite should have an Or content of about 70%. Only at water pressures in excess of 5000 bars would it be possible for a potassium feldspar to

crystallize with the observed Or content. Such a high water pressure is of course compatible with the generally accepted theories on pegmatite genesis.

Summary of trace element results. Summarizing briefly, the trace element data on the Amelia feldspars indicate an order of crystallization of: clevelandite albite, moonstone albite, alkali feldspar. The presence of a late clevelandite is not ruled out but no samples of it are believed to be present among the samples analyzed. The alkali feldspar which crystallized at the end of the above sequence exsolved to yield a microcline containing 20% of the Ab molecule and an albite containing about 3% of the Or molecule. The temperature of the exsolution can be determined from the composition of the albite and microcline (Barth, 1951) to be about 450°C. This would be in accord with the temperature deduced from the perthite classification of Tuttle (1952). Coarse perthite (about 1 mm) was placed by Tuttle on the low temperature end of his classification. According to Tuttle, the coarseness of the perthite also implies a longer time period between crystallization and exsolution. The distribution coefficient k (Barth, 1951) for sodium between the albite and microcline (mole fraction Ab in microcline divided by mole fraction Ab in albite) is about 0.21 which is at the extreme low end of the temperature range. Only alpine type veins had lower k

values. The observed paragenetic sequence also indicates that the water pressure at the time of crystallization must have been in excess of 5000 bars.

Rubidium-Strontium Analyses

As discussed above under Prior Geochronological Work, the geochronological data on the Amelia, Virginia pegmatites are meagre. The K-Ar results on micas from this study yield a mean apparent age of 248 ± 4 m.y. while the results on the albites and microcline are highly discordant. With respect to the mean mica age the albites contain extraneous ^{40}Ar , but unless the meaning of this mean age is determinable it is impossible to say whether the albites contain excess or inherited ^{40}Ar .

In an attempt to clarify the meaning of this 248 m.y. apparent age, Rb-Sr measurements were made on selected samples from the two pegmatites. Isotope dilution analyses were performed on zinnwaldite from the Morefield pegmatite and on albite and microcline separated from the green microcline perthite (AWL-22-65w.r.) from the Rutherford pegmatite. Isotope ratios were determined on the perthite, microcline and five albites. The results of these analyses are given in Table 8. The errors on these analyses are generally large due to unsuitable Sr/Rb ratios. Strontium concentrations were low and in the case of the perthite, microcline and zinnwaldite the rubidium concentrations were

exceedingly high. Errors in the x-ray fluorescence analyses were discussed above and will not be discussed further here. Replicate analyses of the microcline by both isotope dilution and x-ray fluorescence differed markedly suggesting possible sample inhomogeneity. In the isotope ratio measurement of microcline and perthite, considerable difficulty was caused by the interference of ^{87}Rb . Values for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for these two minerals were obtained by plotting 87/86 ratios against 85/86 ratios and projecting back to zero 85/86 or zero rubidium. The values obtained by this method were then normalized in the standard manner. This leads to considerably larger errors in the value of $^{87}\text{Sr}/^{86}\text{Sr}$.

Using a decay constant of $1.39 \times 10^{-11} \text{ yr.}^{-1}$ and assuming an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.711, apparent ages were calculated for two minerals. Zinnwaldite from the Morefield pegmatite gave an apparent age of 272.1 m.y., in close agreement with the mean muscovite Rb-Sr age of 273 m.y. obtained by Deuser and Herzog (1962). Two analyses were made of the microcline (AWL-22-65m) giving apparent ages of 309.4 and 294.9 m.y.

Two isochron plots have been constructed using the results on the Rutherford pegmatite samples. The first of these utilized the microcline perthite and the albite and microcline separated from it. Construction of this isochron

(Figure 6) is based on the assumption that the perthite-albite-microcline assemblage has acted as a closed system since exsolution. Thus the slope of the line yields the time of exsolution, 277 m.y., and the intercept yields the value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, 0.863, at the time of exsolution.

The original time of crystallization may be obtained in several ways. An isochron plot of the perthite, the albites that are believed to have crystallized directly from the melt, and the muscovite of Deuser and Herzog (1962) should yield the time of original crystallization and the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio if these individual minerals have remained closed systems since crystallization. This isochron is shown in Figure 7. Because of the large variations in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the albites the lowest value was used to obtain the maximum age (287 m.y.). The intercept of this line yields an initial ratio of 0.734.

If the initial ratio of the perthite were known the original age of crystallization of the pegmatite could then be obtained from this mineral since it is probable that the whole rock perthite has remained a closed system since crystallization. Redistribution of rubidium and strontium occurred during exsolution but it is believed that the whole rock perthite neither gained nor lost either rubidium or strontium during this process. A maximum age of 292 m.y.

Figure 6. Rb-Sr Isochron of Perthite, Albite, and Microcline, Rutherford Pegmatite

Figure 7. Rb-Sr Isochron of W.R. Perthite, Muscovite, and Albite, Rutherford Pegmatite

is obtained if an initial ratio of 0.704, the value commonly measured in mantle derived basalts, is used.

In Figure 8 the analytical results on the four albites that are believed to have crystallized directly from the melt are shown on the isochron type plot. It is readily seen that the four albites do not yield a unique isochron. Apparently either no single initial ratio was possessed by these samples or there has been redistribution of either rubidium or strontium or both. This is confirmed when the maximum age of 292 m.y. is used in conjunction with the measured $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to calculate the initial ratios. These ratios are shown in Table 9. In Figure 9 and 10 these initial ratios are plotted as functions of the total strontium contents and the order of crystallization as expressed by the K/Rb ratios. Although the agreement is not perfect there is apparently a decrease in the initial ratio with order of crystallization. This may be explained by the assimilation of wall rock with a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the melt. The pegmatitic melt had a high rubidium content as evidenced by the rubidium contents of the microcline and perthite, and a low strontium content. The effects of digestion of wallrock with a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would be magnified in this case. For example if the wallrock had a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710 at the time of digestion and a strontium concentration of 250 ppm, both reasonable assumptions, dilution of the ratios in the pegmatite melt would require digestion

Figure 8. Rb-Sr Isochron Plot of Albites,
Rutherford Pegmatite, Amelia, Virginia

Figure 9. Variation of $(^{87}\text{Sr}/^{86}\text{Sr})_0$ with Order of Crystallization

Figure 10. Variation of $(^{87}\text{Sr}/^{86}\text{Sr})_0$ with Total Strontium Control

Table 9. Results of Rb-Sr analyses on minerals from the Rutherford and Morefield pegmatites, Amelia, Virginia.

Sample Number and Mineral	Rb ppm	<u>Isotope Dilution</u>		$^{87}\text{Rb}/^{86}\text{Sr}$	Apparent Age m.y.
		Sr ppm	$^{87}\text{Sr}/^{86}\text{Sr}$		
AWL-23-65, Zinnwaldite	8327 8358	3.43	27.422	7049	272.1
AWL-22-65m, Microcline	2485	12.58	3.1761	571.9	309.4
AWL-22-65m, Microcline	2588.5	12.75	3.1253	587.7	294.9
AWL-22-65a, Albite	96.70	16.99	0.92657	16.48	--

Table 9. (Continued)

Sample Number and Mineral	<u>X-ray Fluorescence and Isotope Ratio</u>				
	Rb ppm	Sr ppm	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0^*$
AWL-23-65, Zinnwaldite	8471.5 $\pm$ 101.0	4.6 $\pm$ 1.1			
AWL-22-65w.r., Perthite	2313.4 $\pm$ 29.0	14.1 $\pm$ 0.8	2.803 $\pm$ 0.010	516.6	
AWL-22-65m, Microcline	2605.8 $\pm$ 35.0 2443.4 $\pm$ 35.0	12.8 $\pm$ 0.8	3.275 $\pm$ 0.025		
AWL-22-65a, Albite	93.6 $\pm$ 1.4	11.9 $\pm$ 0.6	0.9409 $\pm$ 0.0013		
AWL-25-65, Albite	13.7 $\pm$ 0.7	38.5 $\pm$ 0.6	0.7435 $\pm$ 0.0008	1.034 $\pm$ 0.055	0.7393
AWL-24-65, Albite	27.6 $\pm$ 0.7	49.7 $\pm$ 0.7	0.7402 $\pm$ 0.0002	1.613 $\pm$ 0.047	0.7337
AWL-5-65a, Albite	5.89 $\pm$ 0.62	16.6 $\pm$ 0.6	0.7586 $\pm$ 0.0008	1.033 $\pm$ 0.995	0.7544
AWL-13-65, Albite	4.6 $\pm$ 0.5	28.6 $\pm$ 0.5	0.7433 $\pm$ 0.0006	0.4674 $\pm$ 0.051	0.7414

*Corrected for age of 292 m.y.

of a mass of wallrock equivalent to only about 2% of the mass of the pegmatite. At least a small amount of wallrock digestion is indicated by the development of biotite in the border zone of the pegmatite. Assimilation of the wallrock also readily explains the increase in strontium in the later albites.

There is an alternative explanation for the decrease in the apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with increasing strontium content. If the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was initially low in the melt, then any addition of ^{87}Sr to the albites by a later redistribution would yield higher ratios in the samples with lower total strontium contents. The high rubidium minerals such as microcline could have served as sources for the added ^{87}Sr . Although the alternative is certainly possible no geological evidence for such a later redistribution exists. To call on such an unknown process appears to be unnecessary when evidence is readily available for the assimilation of the wallrock.

Summary and Discussion

As a result of this study considerable data are now available for interpreting the geological, geochemical and geochronological history of the Rutherford and Morefield pegmatites. It is possible to postulate a source for the melt and to trace it through its emplacement to the eventual closing of the system for the daughter isotopes.

The high initial values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate that at least the strontium and probably all the material in the pegmatite melt had a crustal origin. Since the pegmatites are emplaced in a metamorphic terrain it is reasonable to assume that the material had its origin in the anatexis of these metamorphic rocks. The melt formed by this process as indicated by the earlier albites had K/Rb ratios near the crustal average. Widely varying K/Rb ratios in the albites demonstrate that after emplacement the melt differentiated strongly, providing a means of ordering the crystallization of the albites and the perthite. The regular covariance of potassium and rubidium in these samples requires closed system crystallization of the melt with only very limited addition of components from outside the system. Some small amount of assimilation of wallrock is required by the dilution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the albites.

The metamorphic event which produced these pegmatites was apparently of considerable duration. Deuser and Herzog (1962) reported apparent age differences of 28 m.y. between muscovites from the Morefield and Rutherford pegmatites. Although the apparent ages obtained in this study by the Rb-Sr method on zinnwaldite and microcline from the two pegmatites are older than the values of Deuser and Herzog (1962), the difference in time between them is about the

same. Differences in K-Ar and Rb-Sr ages also suggest a long high temperature period. Temperatures in this area must have remained high for tens of millions of years. Such a long period at high temperatures may have contributed to the extreme differentiation shown by the K/Rb ratios and to the coarseness of the perthite.

The apparent ages and trace element data on the Rutherford pegmatite present an excellent picture of the thermal history of this body and the behavior of the daughter isotopes. After crystallization of the five albites analyzed, an alkali feldspar crystallized at about 287 m.y. At this time ^{87}Sr was no longer being exchanged with the melt, the feldspar system was closed. At 277 m.y. the temperature of this feldspar had decreased to a point where exsolution occurred forming the perthite. The compositions of the albite, microcline and perthite serve to fix the temperature at this time as about 450°C . If the temperature of crystallization of the original alkali feldspar were known or could be estimated, then the change of temperature with time could be used to predict the time of closure of the minerals for argon.

Experimental work on the alkali feldspars by Bowen and Tuttle, (1950) and Yoder et al. (1957) indicates that the temperature of crystallization of a single alkali feldspar is strongly dependent upon the water pressure in the

melt. Unfortunately, this pressure is indeterminate for the Rutherford pegmatite although it must have exceeded 5000 bars. An upper limit of about 700°C can probably be placed on the crystallization of the feldspar from the data of the above workers. Recognition of the fact that pegmatitic quartz is almost invariably present as the low temperature form (Jahns, 1955) suggests that it formed below 573°C . Winkler (1965) has presented experimental evidence indicating that anatexis of metamorphic rocks could begin at a temperature of 655°C under 2000 bars of water pressure.

The data cited above suggest that the alkali feldspar probably crystallized between 600°C and 700°C . In Figure 11 a temperature of $650^{\circ} \pm 50^{\circ}\text{C}$ has been assigned to the crystallization of the alkali feldspar. This temperature range has been plotted at a time of 287 m.y. Exsolution at a temperature of 450°C is plotted at 277 m.y. If the time rate of change of temperature is assumed to be constant then the micas would have started to quantitatively retain their argon at a temperature of 160°C . Considering the slow change of temperature with time this is not a bad approximation of the temperature. This should be considered a minimum temperature of closure since the temperature change with time probably decreases at lower temperatures. If so, the temperature of closure would be somewhat above 160°C .

Figure II. Thermal History of Rutherford Pegmatite

It is interesting that the times of closure should be nearly the same for the muscovites and the zinnwaldite despite large differences in the actual grain size. Although values of D have been experimentally measured for phlogopite and biotite, no such measurements are known for either muscovite or zinnwaldite. As pointed out by Damon (1968), however, muscovite is usually more retentive than biotite or phlogopite. Zinnwaldite would be expected to have a value of D close to that of biotite. Thus if the diffusion distances were similar for muscovite and zinnwaldite, the zinnwaldite should yield a younger age. The larger grain size of the zinnwaldite may, however, indicate a larger diffusion distance which would tend to minimize the effect of the larger value of D in the zinnwaldite.

With the geochronology of the Rutherford and Morefield pegmatites known, it is now possible to interpret the anomalous K-Ar results obtained on the albite, topaz, quartz and beryl. The results must be considered with respect to the times of closure of the individual minerals for strontium and argon.

Let us first consider the results obtained on the five albites from the Rutherford pegmatite. All five of these samples yield apparent ages greater than the mean mica age of 248 m.y. If, however, the Rb-Sr data are correct, then only three of the samples contain excess

^{40}Ar . The other two samples are essentially concordant with the 287-292 m.y. age.

If the five samples of albite are placed in the order of crystallization as determined by trace element evidence, the ages are 283, 384, 297, 352, and 445 m.y. corresponding to excess ^{40}Ar contents of 0.0, 0.281, 0.0, 0.294, and 1.348×10^{-10} m/g respectively. Although the correlation is not perfect because of the third sample, the excess ^{40}Ar contents apparently increase with order of crystallization. This should be expected if the system was closed to argon allowing the partial pressure of argon to increase as crystallization proceeded.

It is possible to imagine several ways whereby the argon partial pressure would increase during crystallization. First, it is likely that the total pressure in the melt would increase during crystallization. This is simply a result of the decreasing volume available for the volatiles as the pegmatite crystallizes from the walls inward. That such a pressure buildup commonly occurs in pegmatites is evidenced by fractures, often filled with sugary albite, that lead outward from the inner zones of pegmatites. This albite evidently results from rapid crystallization as the volatiles escape from the uncrystallized central portion of the body. Such fractures were observed for example, in the pegmatite from the White Picacho district, Arizona.

The partial pressure of argon could also increase in response to changes in the mole fraction of argon in the volatiles. The bulk of the volatiles present in the melt is undoubtedly H_2O . Damon (1957) for example, found that in beryl 72-75% of the incorporated gases was H_2O . Crystallization of a large quantity of a hydrous phase such as muscovite could greatly change the composition of the volatile phase and hence the mole fraction of argon. As the mole fraction of argon in the volatiles increases so also should the quantity of excess ^{40}Ar incorporated by the mineral.

Damon (1957) observed systematic variations in the excess argon and helium contents of a single beryl crystal from the Beryl Mountain pegmatite. In this case the argon partial pressure apparently decreased with crystallization while the helium contents showed an increase followed by a decrease.

The blue albite from the Morefield pegmatite clearly contains excess ^{40}Ar yielding an anomalous age of 416 m.y. With respect to the mean mica age this is an excess of 0.570×10^{-10} m/g, while if the age of the zinnwaldite is used the sample contains 0.493×10^{-10} m/g of excess ^{40}Ar . The samples of quartz, topaz and beryl also clearly contain excess ^{40}Ar .

In this work the values of D/r^2 for the Rutherford microcline have been measured over the temperature range 375-600°C. Knowing these values and utilizing the proposed cooling curve (Figure 11) for the Rutherford pegmatite it is possible to predict the time of closure of the microcline for argon loss. To obtain this time the following equation of Damon (1968) was used:

$$^{40}\text{Ar}/^{40}\text{K} = \frac{\lambda_K}{\lambda_d - \lambda} \exp(\lambda t_C) [\exp(-\lambda t_B) - \exp(-\lambda_d t_B)] + \frac{\lambda_K}{\lambda} [\exp(\lambda t_R - 1)] + \frac{^{40}\text{Ar}_O}{^{40}\text{K}} \exp(-\lambda_d t_B)$$

Where λ_K = decay constant for K by electron capture
 λ = total decay constant for K
 λ_d = diffusional escape constant
 t_C = time of original crystallization
 t_B = time of burial at elevated temperature
 t_R = time of refrigeration

This equation is applicable to the general case where a mineral crystallizes at a time t_C , remains at a temperature sufficiently high to allow argon diffusional loss for a period of time t_B and is then uplifted at time t_R to an elevation where the temperature is low enough for complete argon retention.

The above equation was evaluated, assuming that t_C was equal to 290 m.y., at $t_R = 270, 250$ and 230 m.y. using the appropriate temperatures and values of D/r^2 . Assuming a spherical diffusion model (Damon, 1968) at 270 and 250

m.y. the $^{40}\text{Ar}/^{40}\text{K}$ ratio would be equal to zero. Retention of ^{40}Ar by the microcline would only commence at a time of about 230 m.y. and a temperature of about 150°C . The results of these calculations are in good agreement with the measured microcline ages of 213-231 m.y. It thus is evident that the measured values of D/r^2 are adequate to explain the observed losses for these potassium feldspars.

CHAPTER IV

PEGMATITE FROM THE WHITE PICACHO DISTRICT, ARIZONA

The following resume of the geology of the White Picacho District, Arizona is taken from the work of Jahns (1952) and from field observations made during the summer of 1966.

Location and Geologic Setting

The White Picacho District lies in the southern part of the Arizona pegmatite belt. This belt, which is about 250 miles long and 30 to 80 miles wide, extends south-southeast from Lake Mead to south of Phoenix. The White Picacho District makes up about 150 square miles in Maricopa and Yavapai Counties.

The pegmatites within this district intrude Precambrian igneous and metamorphic rocks and locally are covered by Tertiary and Quaternary sedimentary and volcanic rocks. Granitic rocks are abundant in the district, especially in the northern portion. The most typical granite is gray, medium to coarse grained, and may be slightly porphyritic. The metamorphics are part of the Yavapai schist and are the oldest rocks in the area. The pegmatites

occur in both the Yavapai and the granite, being in general, smaller and more irregular in the granite.

Three types of pegmatites occur in the district. The first and most abundant are simple pegmatites composed of quartz, potassium feldspars and minor plagioclase and muscovite. Accessory minerals include biotite, garnet, beryl, and black tourmaline (schorl). The second type is similar in bulk composition to the first but has a more varied mineral assemblage. It is also distinguished by a central zone of coarse grained quartz and/or potassium feldspar. This core may contain crystals up to tens of feet in length. The third type of pegmatite is lithium rich, with the lithium minerals generally concentrated in the core.

Structurally the pegmatites are generally elongate, very irregular, and distinctly discordant. They trend N. to N.E. or E.N.E. to E. and dip steeply. Almost all of the pegmatite-wallrock contacts are sharp and many are highly irregular. There is little alteration of the wallrock. Most of the pegmatites are zoned. In general, the border zones are fine to medium grained and range in thickness from 1/8 inch to several feet. They consist largely of quartz, albite, tourmaline and perthite. The wall zones are more continuous and better defined than the border zones. They average between three and eight feet thick and consist

of fine to coarse grained perthite, subordinate plagioclase, schorl and mica. There may be accessory garnet, apatite, beryl, and spodumene.

The intermediate zones are more irregular and still less complete. They are composed of perthite, quartz, plagioclase and a variety of lithium minerals. The quartz content and the grain size increase toward the core.

The cores are the most variable zones in form, position, texture, and mineralogy. Mineralogically they may range from simply quartz to varied lithium mineral assemblages.

Jahns (1952) suggests that the pegmatite forming solutions were injected along fractures, contacts, and bedding and foliation planes. Since there is abundant evidence of forceful injection and progressive crystallization from the walls inward, Jahns felt that replacement processes were of minor importance in this district.

The pegmatite supplying the samples used in this study is exposed in a vertical cut on the hillside north of the abandoned mica mill in San Domingo Wash (Figure 12). It is enclosed by and in fault contact with Yavapai schist. As are most of the pegmatites in the area, this pegmatite is well zoned. Although spodumene was the only lithium mineral recognized, its abundance places the pegmatite in

Figure 12 Location Map, White Picacho District, Arizona

the type three of Jahns (1952). Since the excavation was very recent all samples analyzed were fresh and unaltered.

Prior Geochronological Work

Only two prior dates exist for pegmatites in the White Picacho district. Aldrich et al. (1958) report a K-Ar age of 1160 m.y. and a Rb-Sr age of 1300 m.y. on a muscovite from a pegmatite near Wickenburg.

Analytical Results

Potassium-Argon Analytical Results and Discussion

Four mineral samples from this pegmatite were analyzed for both potassium and argon. Two additional albite samples were potassium analyzed as part of an investigation of the trace element content of pegmatitic albites. The results of these analyses are given in Tables 10 and 11. The first sample analyzed was a coarse grained muscovite from near the center of the pegmatite. This sample furnished a comparison age of 1270 ± 40 m.y. for the low potassium minerals. Spodumene separated from a large crystal associated with the muscovite had a potassium content of 0.45% and gave apparent ages of 1580 ± 50 m.y. and 1600 ± 50 m.y. by duplicate argon analyses. In the border zone coarse grained albite is cut by veins up to one inch wide of sugary albite. The two types of albite were carefully separated

Table 10. Pegmatite, White Picacho District, Arizona.

<u>Reference Ages</u>					
Mineral	Age m.y.	Method	Reference		
Muscovite	1160	K-Ar	Aldrich et al., 1958		
Muscovite	1300	Rb-Sr	Aldrich et al., 1958		
<u>New Data</u>					
Sample Number and Mineral	K %	⁴⁰ Ar radiogenic x 10 ⁻¹⁰ m/g	⁴⁰ Ar atmos. %	Apparent Age m.y.	Apparent Excess ⁴⁰ Ar x 10 ⁻¹⁰ m/g
AWL-16-66, Muscovite	8.32 ±.04 8.31 ±.03	270.0	1.9	1270±40	--
AWL-19-66C, Albite	0.538±.005 0.535±.004	9.754	1.0	816±24	--
AWL-19-66F, Albite	0.35 ±.01 0.34 ±.01	5.687	2.6	754±23	--
AWL-15-66, Spodumene	0.45 ±.01 0.45 ±.01	20.19 19.75	14.1	1580±50	--

Table 11. Potassium, rubidium, and strontium contents of albites from pegmatite, White Picacho District, Arizona.

Sample Number	K %	Rb ppm	Sr ppm	K/Rb	Rb/Sr
AWL-18-66	0.091	14.1 $\pm$ 0.52	7.26 $\pm$ 0.44	64.5	1.94
AWL-20-66	0.1085	30.2 $\pm$ 0.58	29.9 $\pm$ 0.48	35.9	1.01
AWL-19-66F	0.345	276.7 $\pm$ 2.4	9.95 $\pm$ 0.45	12.4	27.8
AWL-19-66C	0.537	493.5 $\pm$ 4.2	11.3 $\pm$ 0.46	10.9	43.7

and analyzed. The large crystals gave an apparent age of 816 ± 24 m.y. while the sugary albite gave a lower apparent age of 754 ± 23 m.y.

The significantly younger ages on the two albite samples suggest that this pegmatite was reheated subsequent to its emplacement. Such a later thermal perturbation is also in accord with the grain size effect noted in the ages of the albite samples. The true age of emplacement of the pegmatite cannot be stated with certainty. Since the albites have clearly lost argon it is likely that some loss has also occurred in the muscovite. If so, the pegmatite was of course emplaced prior to the 1270 m.y. date. An older age would agree more closely with the major periods of Precambrian batholithic activity in Arizona. These

periods are at about 1400 m.y. and between 1600-1700 m.y. (Livingston and Damon, 1968).

The high age on the spodumene sample might be explained in several ways. First, this may be near the true age of emplacement, little argon loss occurring because of high retention of the mineral and the large diffusion distance. Secondly, because of the low potassium content of the sample, the possibility of excess argon must be considered. If excess argon was incorporated by the spodumene at the time of its crystallization, then the true age of the pegmatite would lie somewhere between 1270 and 1600 m.y. A third possibility would be that excess argon was originally incorporated by the spodumene and that later argon loss occurred upon heating. It is obvious that no definite information can be obtained on the actual time of emplacement from the spodumene data.

The later heating was probably caused by the deposition of Cretaceous and Tertiary volcanics. Although they were not present in the immediate vicinity they are present several miles both upstream and downstream from the pegmatite. Tectonic activity as manifested in the several faults cutting the pegmatite may also have caused partial degassing of the samples.

Trace Element Analytical Results and Discussion

The potassium, rubidium and strontium contents of four albites were measured to determine if the relationships observed in the Rutherford pegmatite and the Landsverk pegmatite held true for other pegmatites. The results of these analyses are given in Table 11 and Figure 13.

Samples AWL-19-66 C and F and AWL-20-66 were collected from the border zone of the pegmatite; 19-66C and F from the floor of the pegmatite and 20-66 from the west end. Two generations of albite were present in AWL-19-66. A coarse grained fraction, designated by the letter "C", was typical of the border zone. This coarse albite was cut by veins of sugary albite ("F") about one inch wide apparently coming out of the intermediate zones in the pegmatite. The sugary albite has entered fractures in the earlier minerals and has replaced and reacted with them. Tourmaline crystals (schorl) are locally concentrated along the small veins. Separation of the two types of albite for analysis was difficult. The sugary albite separate (AWL-19-66F) is believed to be pure and free of contamination by the coarse albite. Because of penetrations and replacements of the sugary albite, the coarse albite undoubtedly contains some of this finer grained albite.

The sample AWL-18-66 was collected near an inclusion of Yavapai schist above the muscovite-spodumene zone.

Figure 13. K vs. Rb for Albites from Pegmatite,
White Picacho District, Arizona

The albite was present as coarse crystals with abundant associated schorl. Several inclusions of Yavapai schist occur in the pegmatite and invariably they were rimmed with the black tourmaline-coarse albite-potassium feldspar assemblage typical of the border zone of the pegmatite.

The range in time of crystallization between AWL-19-66C, 18-66, and 20-66 is probably not great. All three samples were from the same mineral assemblage, black tourmaline-coarse albite-potassium feldspar. This black tourmaline may indicate extraction of iron from the Yavapai schist wallrock and inclusions. The sugary albite (AWL-19-66F) is clearly later than the coarse albite with which it is associated since it occurs in veins cutting the coarse crystals. Crystallization of this fine grained material probably took place as a result of loss of volatiles due to fracturing of the pegmatite. These fractures tapped still liquid material in the intermediate zones or core and allowed it to escape and react with the earlier albite and potassium feldspars.

The potassium and rubidium contents of the three samples from the border zone and adjacent to the inclusion vary widely as evidenced by the K/Rb ratios ranging from 64.5 to 10.9. The sugary vein albite has potassium and rubidium contents that fall between the extremes of the other samples. On a log-log plot of potassium content

vs. rubidium content (Figure 13), the four samples yield a straight line defined by the equation $\log Rb(\text{ppm}) = 3.185 + 1.799 \log K\%$. The fit of this line is not so good as that for the Rutherford and Landsverk pegmatites, however, the three pegmatites do give lines with approximately the same slope. It is disturbing though, that the results on the sugary albite (AWL-19-66F) fall within the extremes of the other three samples. This sample is clearly later than AWL-19-66C and yet it has lower potassium and rubidium contents and a higher K/Rb ratio than this sample. Textural evidence indicates that the system has opened before crystallization of the sugary albite. The solution or melt from which this albite crystallized has also clearly reacted with the earlier crystals. The opening of the system and reaction with the earlier crystals may not allow direct comparison with the other pegmatites. Both processes could lead to displacements of a sample along the line of differentiation.

Two lines of evidence suggest that the melt from which this pegmatite crystallized was highly fractionated. Border zone albite K/Rb ratios are exceedingly low; the highest measured is only 64.5. Thus, the melt was highly fractionated even before crystallization of the border zone albite. This is in contrast with the Rutherford pegmatite where albites have K/Rb ratios very near the crustal

average. The presence of tourmaline in the border zone indicates that the volatile content was high enough at that stage of crystallization for the tourmaline to form. In the Rutherford pegmatite, biotite in the wall and border zones acts in the same fashion as tourmaline in the White Picacho pegmatite, i.e., accepting iron from the wall rock.

CHAPTER V

EVALUATION OF THE EXCESS INERT GAS AGE EFFECT IN PLAGIOCLASE

Damon and Kulp (1958) observed that in the cyclosilicates, beryl, tourmaline and cordierite, the quantity of excess argon and helium increased with the known age of the sample. It was suggested that this resulted from higher argon pressures at the time of crystallization of older samples. As was shown in Figure 1, if the level of excess argon remains constant, then the apparent age will approach the true age as the true age increases. If, however, the excess inert gas age effect is also present in minerals other than the cyclosilicates it will be impossible to say if or when the effect of the excess argon becomes negligible.

To evaluate this phenomenon, cogenetic mica-plagioclase pairs were analyzed from a number of pegmatites of widely varying ages. Results of these analyses are shown in Tables 12-22. Each of the localities will be discussed below and supporting geochronological data will be presented where available.

Chemalloy Pegmatite, S. E. Manitoba

The following description of the Chemalloy pegmatite is taken from the work of Hutchinson (1959). This pegmatite, formerly known as the Montgary pegmatite, is located near Bernic Lake in the southeastern Manitoba pegmatite district. It is a complexly zoned, lithium rich, sill-like pegmatite striking northwestwardly and dipping 15° to the north-northeast. The thickness varies from 60-200 feet over a diameter of 1500 feet.

The pegmatite is enclosed by massive hornblende-plagioclase gneisses or amphibolites which strike $N90^{\circ}E$ and dip steeply to the south. The contacts with the metamorphics are sharp and tourmalinized. Xenoliths are present and are commonly tourmalinized. The xenoliths may be rimmed by a chill zone of plagioclase one half inch thick.

Hutchinson (1959) recognized eight distinct zones within the pegmatite. These range from an outermost zone of perthite, plagioclase, quartz and muscovite through a series of lithium-rich zones to a quartz core. The zoning, sharp contacts, tourmalinization, and crystal growth perpendicular to the contacts led Hutchinson to conclude that the pegmatite was emplaced in the fluid state. He did, however, suggest that the aplitic albite, lepidolite-albite, and pollucite assemblages resulted from replacement during a late stage of pegmatite development. He suggests that the

source of the replacing solutions, which had to be rich in sodium, cesium and lithium, was exsolution from early feldspars, or, alternatively, residual solutions after late crystallization.

Prior Geochronological Work

Although no radiometric ages have been reported on the Chemalloy pegmatite itself, numerous ages have been determined on other pegmatites in the area. In particular the pegmatite at the Silverleaf Mine has been extensively dated. These data as well as data from the Huron claim are summarized in Table 12. The general concordance of the apparent ages indicates that the emplacement of the pegmatites took place about 2500 m.y. ago.

Analytical Results and Discussion

Five mineral separates were analyzed from the Chemalloy pegmatite. The results of these analyses are given in Table 13. The reference age was established by the analysis of a lepidolite sample which gave an apparent K/Ar age of 2450 ± 70 m.y. This result is in good agreement with results on other pegmatites from this area. Albite separated from the same sample had a potassium content of 0.147% and gave an apparent age of 2880 ± 90 m.y. Quartz, also from the same sample, had a very high potassium content of 0.134% and yielded an apparent age of

Table 12. Chemalloy pegmatites.

Pegmatite	Mineral	Reference Ages		Reference
		Method	Age (m.y.)	
Silverleaf Mine	Lepidolite	K/Ar	2480	Lowdon (1960)
	Lepidolite	K/Ar	2550 $\pm$ 150	Cummings (1955)
	Lepidolite	K/Ar	2177 $\pm$ 150	Stevens and Shillibeer (1956)
	Muscovite	K/Ar	2160	Aldrich et al. (1958)
		Rb-Sr	2640	
	Lepidolite	K/Ar	2440 $\pm$ 60	Gast, Kulp and Long (1958)
		Rb-Sr	2680 $\pm$ 90	
	Lepidolite	Rb-Sr	2670 $\pm$ 67	Gast et al. (1958)
	Microcline	Rb-Sr	2340 $\pm$ 140	Gast et al. (1958)
Huron Claim	Lepidolite	K-Ar	2286	Cummings (1955)
	Muscovite	K-Ar	2153 $\pm$ 155	Stevens and Shillibeer (1956)
	Uraninite	U-Pb,Th-Pb	1360 - 2505	Eckelmann and Kulp (1957)
	Monazite	U-Pb,Th-Pb	1830 - 3180	Nier, Thompson and Murphey (1941)
	Uraninite	U-Pb,Th-Pb	1252 - 2200	Nier (1939)
	Mica	K-Ar	2148	Shillibeer and Cummings (1956)

Table 13. Potassium-argon analyses, Chemalloy pegmatite, Manitoba.

Sample Number and Mineral	K %	^{40}Ar $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %	Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
AWL-27-65L, Lepidolite	7.33 ± 0.04 7.33 ± 0.06	657.7	0.8	2450 $\pm$ 70	--
AWL-27-65a, Albite	0.147 ± 0.004 0.147 ± 0.006	17.93	1.0	2880 $\pm$ 90	4.74
AWL-26-66, Albite	0.233 ± 0.001 0.236 ± 0.001	19.48	3.5	2340 $\pm$ 70	--
AWL-27-66, Spodumene	0.0055 $\pm$ 0.0007 0.0057 $\pm$ 0.0005	2.764	1.4	5160 $\pm$ 150	2.26
AWL-27-65Q, Quartz	0.132 ± 0.001 0.135 ± 0.001	13.65	4.7	2630 $\pm$ 80	1.67

2630 $\pm$ 80 m.y. A second albite sample had a slightly higher potassium content (0.235%) and gave an apparent age of 2340 $\pm$ 70 m.y., indistinguishable from the lepidolite age. A sample of spodumene from a giant crystal had an extremely low potassium content (0.0056%) and gave an apparent age of 5160 $\pm$ 150 m.y.

If the lepidolite age of 2450 $\pm$ 70 m.y. is considered the true time of emplacement of the Chemalloy pegmatite, then the older albite, spodumene and quartz ages may be readily explained by the incorporation of excess argon at the time of crystallization. These minerals would require the incorporation of 4.74×10^{-10} , 2.26×10^{-10} , and 1.67×10^{-10} moles/gram respectively of excess argon. The concordant albite age could result from loss of argon, or crystallization after a pressure release of the volatiles in the pegmatites. It is impossible from the available evidence to choose between these alternatives.

Pegmatites in Granodiorite, Monte Capanne, Elba

The granodiorite which makes up the Monte Capanne on the island of Elba is one of the oldest intrusives in the Tuscan Archipelago (Eberhardt and Ferrara, 1962). These authors consider it to be post-upper Eocene and pre-upper Miocene on the basis of stratigraphic evidence. It is a medium grained rock with an idiomorphic texture and is

composed primarily of andesine, orthoclase, quartz and biotite.

The intrusive contains numerous pegmatites in the marginal facies, (Bonatti, 1965) (Figure 14). These veins occasionally open into cavities which have been mined in the past for their beryl, tourmaline, feldspars, and zeolites.

Prior Geochronological Work

The granodiorite itself and its included pegmatites have been dated by both the K-Ar and Rb-Sr methods by Eberhardt and Ferrara (1962), and Ferrara et al. (1961). Their results are given in Table 14. The average Rb-Sr age of the biotite from the granodiorite is 10.1 m.y. while the K-Ar age is 7.6 m.y. The pegmatite minerals give average ages by the Rb-Sr method of 6.4 m.y. (Eberhardt and Ferrara, 1962) and 6.8 m.y. (Ferrara et al., 1961). One sample of lepidolite gave a K-Ar age 6.4 m.y. (Eberhardt and Ferrara, 1962).

Analytical Results and Discussion

A sample of biotite from the granodiorite and samples of tourmaline and albite from the pegmatites were analyzed in this study. The results of these analyses are given in Table 14. The sample of biotite gave apparent K-Ar ages of 8.59 ± 2.23 m.y. and 7.38 ± 0.22 m.y. in good

Figure 14. Location Map, Pegmatites, S. Piero, Elba

Table 14. Pegmatites in granodiorite, Monte Capanne, Elba.

Mineral and Rock	<u>Reference Ages</u>		References
	Age m.y.	Method	
Biotite, granodiorite	10.4	Rb-Sr	Ferrara et al., 1961
Biotite, granodiorite	7.6	K-Ar	Eberhardt and Ferrara, 1962
Biotite, granodiorite	9.8	Rb-Sr	" " " "
2 Pollucite, pegmatite 4 Lepidolite	6.8 Av.	Rb-Sr	Ferrara et al., 1961
2 Pollucite, pegmatite 4 Lepidolite	6.4 Av.	Rb-Sr	Eberhardt and Ferrara, 1962
Pink lepidolite, pegmatite	7.6	K-Ar	Eberhardt and Ferrara, 1962

Table 14. (Continued)

Mineral and Rock	K %	<u>New Data</u>		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
Biotite, granodiorite	6.94 $\pm$ 0.05	1.059	91.7	8.59 $\pm$ 2.23	--
	6.96 $\pm$ 0.05	0.9158	45.7	7.38 $\pm$ 0.22	--
Tourmaline, pegmatite	0.306*	0.1406	76.2	25.7 $\pm$ 2.0	0.107
Albite, pegmatite	0.300 $\pm$ 0.001	0.1374	41.0	25.5 $\pm$ 0.8	0.0916
	0.302 $\pm$ 0.002				

*Low level beta counting.

agreement with the results from Bern and Pisa. The pegmatitic tourmaline gave a K-Ar apparent age of 25.7 ± 2.0 m.y. and the albite gave an apparent age of 25.5 ± 0.8 m.y.

Using the K-Ar biotite age from this work as the true age the tourmaline has an excess argon content of 0.107×10^{-10} m/g and the albite 0.0916×10^{-10} m/g. These quantities are low for an intrusive environment and approach the values for the extrusive environment reported by Damon et al. (1967).

It is evident from the potassium-argon ages obtained on the biotite from the Monte Capanne granodiorite that this mineral incorporated little or no excess ^{40}Ar at the time of its crystallization. If the biotite had incorporated the same quantity of excess ^{40}Ar as did the albite and tourmaline, it would be about 0.75 m.y. too old. This is not the case since in fact the potassium argon apparent age is less than the rubidium-strontium age. From the rubidium-strontium ages of the granodiorite and the pegmatites it is possible to place limits on the quantity of excess ^{40}Ar that was incorporated by the biotite. It is impossible for the biotite to be younger than the mean rubidium-strontium pegmatite age of 6.56 m.y. If this age was correct then the biotite would be 1.3 m.y. too old.

Thus the biotite must have incorporated less than 0.15×10^{-10} m/g of excess ^{40}Ar .

Prosperous Lake Pegmatite, Yellowknife Area,
N.W.T., Canada

The Prosperous Lake pegmatite is located on the S.E. bay of Prosperous Lake, N.W.T., Canada at a latitude of $62^{\circ}32'12''$ N. and a longitude of $114^{\circ}08'32''$ W. The pegmatite is enclosed by a garnet-bearing member of Division C of the Yellowknife Group (Canada Department of Mines and Resources Map 868A). It lies south of and is presumably related to the Prosperous Lake granite (Figure 15). According to Lowdon (1961) the Prosperous Lake granite is actually a quartz monzonite with a medium grain size. It is composed of quartz, oligoclase, microcline, muscovite, biotite and accessory apatite. The northern portion of the granite is intruded by E.N.E. striking dikes of olivine and quartz gabbros which are up to 350 feet in width.

The pegmatite is lithium rich and contains microcline, clevelandite albite, muscovite, tourmaline and spodumene. The spodumene occurs as crystals up to three feet in length and comprising up to 5% of the pegmatite.

Prior Geochronological Work

Prior to this work, the pegmatite age was not known although radiometric ages exist for other rocks in the area. Green, Baadsgaard and Cumming (1968) report a whole rock

Figure 15. Geologic and Location Map, Prosperous Lake Pegmatite, N.W.T., Canada

Rb-Sr isochron age of 2500 ± 60 m.y. for Archean greenstones in the Yellowknife area. They also report a Rb/Sr mineral isochron age of 2390 ± 50 m.y. for the Prosperous Lake granite with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710. Lowdon (1961) reports a K/Ar age of 2540 m.y. on muscovite from the Prosperous Lake granite. The basic dikes intruding the granite yield K/Ar apparent ages of 900-1930 m.y. on whole rock samples and 2310 m.y. on a hornblende sample (Payne et al., 1965). The Rb/Sr age on the granite is appreciably younger than the K/Ar age. The samples used for the Rb/Sr dating were apparently collected much closer to the basic dikes, however, and there may have been some migration of rubidium and/or strontium.

Analytical Results and Discussion

The analytical results on samples from the Prosperous Lake pegmatite are given in Table 15. A coarse grained muscovite was first dated to provide a reference age for the pegmatite. This sample had an apparent age of 2530 ± 80 m.y. in excellent agreement with Lowdon's K/Ar age of 2500 m.y. for the nearby Prosperous Lake granite. Intrusion of the granite and emplacement of the pegmatite are clearly indistinguishable. Two low potassium minerals were then analyzed. A fine grained albite with a potassium content of 0.137% gave an apparent age of 1390 ± 40 m.y. This apparent age would result from the loss of 61.5% of

Table 15. Prosperous Lake pegmatite, Yellowknife area, N.W.T., Canada.

Rock	<u>Reference Ages</u>		
	Age m.y.	Method	Reference
Prosperous Lake Granite	2390±50	Rb-Sr (mineral isochron)	Green et al. (1968)
Prosperous Lake Granite (Muscovite)	2540	K-Ar	Lowdon (1961)
Archaen Greenstones	2500±60	Rb-Sr (W.R. isochron)	Green et al. (1968)
Basic dikes (W.R.)	900±1930	K-Ar	Payne et al. (1965)
Basic dikes (hornblende)	2310	K-Ar	Payne et al. (1964)

Table 15. (Continued)

Mineral	K %	<u>New Data</u>		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
Muscovite	8.43 $\pm$.04	808.0	0.4	2530 $\pm$ 80	--
	8.46 $\pm$.04				
Albite	0.137 $\pm$.003	5.021	0.0	1390 $\pm$ 40	--
	0.137 $\pm$.003				
Spodumene	0.52 $\pm$.01	23.34	0.5	1600 $\pm$ 50	--
	0.51 $\pm$.02				
	0.52 $\pm$.01				
	0.53 $\pm$.01				

the radiogenic argon produced by the potassium in 2530 m.y. A sample of spodumene had a potassium content of 0.52% and gave an apparent age of 1600 ± 50 m.y., indicating a loss of 53.1% of the radiogenic argon.

An explanation for the low albite and spodumene apparent ages is not readily available. No basic dikes are reported from the vicinity of the pegmatite. It is possible, of course, that a basic dike not exposed at the surface has perturbed the system. In the case of the spodumene, one possibility not generally considered is the addition of potassium after crystallization. Jahns (1952) has demonstrated that as spodumene weathers it loses lithium and takes up potassium. This would yield an anomalously young age. Since both the albite and spodumene give young apparent ages, however, the most likely explanation is still a later thermal event.

White Queen Pegmatite, Pala District, California

The White Queen pegmatite is one of about 400 pegmatites that occur in the Pala District, San Diego County, California. This pegmatite is located near the center of Hiriart Mountain, northeast of the town of Pala (Jahns, 1951, Plate 2). The geology of the Pala pegmatites, long noted for their gem and lithium minerals, has been thoroughly discussed by Jahns (1951). The following description of the geology is taken from their work.

The country rock of the Pala District is a crystalline complex composed primarily of igneous rocks of the Cretaceous southern California batholith. The more basic members of the batholithic complex are most abundant within the district. The most common of these is the San Marcos gabbro which includes a variety of gabbros and norites. Although the pegmatites intrude all of the rocks in the area and thus are the youngest intrusives, they are most abundant in the gabbros. The pegmatites are emplaced along fractures generally dipping to the west. On Hiriart Mountain they are closely spaced and the pegmatites project above the surface as rib-like structures. The pegmatites commonly split and converge and may tongue into the country rock.

The pegmatites which are complexly zoned have furnished a wide variety of the gem and lithium minerals. The White Queen has been a producer of spodumene, beryl and quartz.

No post-batholithic igneous rocks that could have perturbed age relations are known in this district. Structural activity is still going on in the area, however. Between 3000 and 4000 feet northeast of White Queen pegmatite is the Elsinore fault zone. This is a large fault zone one-half to one mile wide striking northwestwardly and it is characterized by many earthquake epicenters along its length.

Prior Geochronological Work

No previous radiometric ages have been reported for minerals of the White Queen pegmatite. Three other pegmatites from the Pala district have been dated, however. Aldrich et al. (1956, 1958) report a K/Ar age of 89 m.y. and Rb-Sr ages of 106 and 114 m.y. on a lepidolite from a pegmatite from Pala, while Herzog (1961) reports four Rb-Sr analyses by different laboratories on a lepidolite from the Pala mine. These results are 100, 105, 107 and 120 m.y. The M.I.T. results (120 m.y.) were about 100 ppm low in the ^{87}Rb value and should probably be disregarded. Rouse and Mathews (1961) report K-Ar ages ranging from 89 to 96 m.y. on perthite and lepidolite from the Stewart Mine. It thus appears that the Pala pegmatites were emplaced about 100 m.y. ago.

Analytical Results and Discussion

Three samples were analyzed from the White Queen pegmatite. The results are shown in Table 16. A sample of muscovite was first run to establish a reference age for the pegmatite. Duplicate argon analyses yielded ages of 96.1 ± 2.9 m.y. and 98.4 ± 3.0 m.y. in good agreement with other pegmatites in the district. A sample of clevelandite albite with a low potassium content gave an apparent age of 51.1 ± 5.1 m.y. Cogenetic quartz when beta counted did not count

Table 16. White Queen pegmatite, Pala District, California.

Mineral	Location	<u>Reference Ages</u>		References
		Age m.y.	Method	
Lepidolite	Pala, Calif.	89 106-114	K-Ar Rb-Sr	Aldrich et al. (1956) (1958)
Lepidolite	Pala Mine	120 107 100 105		Herzog (1961)
Perthite	Stewart Mine	96±3 89±3	K-Ar	Rouse and Mathews (1961)
Lepidolite	Stewart Mine	94±3 89±3	K-Ar	Rouse and Mathews (1961)

Table 16. (Continued)

Sample Number and Mineral	K %	<u>New Data</u>		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
AWL-23-66, Muscovite	8.59 ± 0.09	15.00	6.0	96.1 ± 2.9	--
	8.53 ± 0.05	15.37	2.6	98.4 ± 3.0	--
AWL-24-66, Albite	0.126 ± 0.002	0.1159	81.0	51.1 ± 5.1	--
	0.126 ± 0.002				
AWL-25-66, Quartz	0.0*	0.0396	70.8	--	0.0396

*Low level beta counting.

above the starch background but contained 3.96×10^{-12} m/g of ^{40}Ar .

If the muscovite age is the true age of emplacement of the White Queen pegmatite, the albite obviously contains no excess argon. In fact, if no excess was incorporated by the albite at the time of its crystallization, then it has lost 48.2% of its radiogenic argon. If the potassium determination of the quartz is correct then the 3.96×10^{-12} m/g of ^{40}Ar must be regarded as excess. This apparent excess must be regarded with skepticism, however, because only 0.02% potassium would generate 3.55×10^{-12} m/g of ^{40}Ar since emplacement and the potassium content could be in error by this amount.

Pegmatite, Bobruvka, Nove Mestona, Morave,
Western Moravia, C.S.S.R.

Two samples from a pegmatite from western Moravia, C.S.S.R. were analyzed during this study. No geological data or prior geochronological results were available for this pegmatite. The samples were of muscovite and albite crystals from an extremely vuggy pegmatite. The analytical results on these samples are given in Table 17.

The analytical data on the Moravian samples show that the albite has lost argon relative to the muscovite. If no excess argon was incorporated by the albite at the

Table 17. Analytical results on pegmatite from Western Moravia, C.S.S.R.

Sample Number and Mineral	K %	^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %	Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
AWL-28-65m, Muscovite	8.67 ± 0.02 8.66 ± 0.02	54.74	2.0	326 ± 10	--
AWL-28-65a, Albite	0.1654 ± 0.0005 0.1653 ± 0.0004	0.8171	45.8	260 ± 10	--

time of its crystallization then the albite has lost 21.6% of its radiogenic argon.

Christmas Lake Pegmatite, Beartooth Mountains, Montana

The Christmas Lake pegmatite is located in the southern Beartooth Mountains of Montana and Wyoming near the border between the two states. It is a zoned pegmatite about 100 feet long and 10 feet wide, conformable with the enclosing Precambrian gneisses (Gast et al., 1958).

Prior Geochronological Work

Several mineral samples from the Christmas Lake pegmatite have been dated by the model lead, Rb-Sr and K-Ar methods. These results are presented in Table 18. The true age of the pegmatite is probably about 2750 ± 50 m.y. with the muscovite showing a slight argon loss.

Analytical Results and Discussion

As part of this study, three samples from the Christmas Lake pegmatite were analyzed. A coarse grained muscovite sample was first analyzed for comparison with the results of other workers. This sample gave an apparent age of 2500 ± 80 m.y., somewhat lower than the reference age. A sample of quartz contained 0.014% potassium and 7.424×10^{-10} m/g of ^{40}Ar . On the basis of the muscovite age, the quartz would contain 6.167×10^{-10} m/g of excess ^{40}Ar and slightly less if the 2750 m.y. age is used.

Table 18. Christmas Lake pegmatite, Beartooth Mountains, Montana.

Mineral	Age m.y.	<u>Reference Ages</u>	
		Method	Reference
Feldspar	2700	Model Lead	Catanzaro and Gast (1960)
Muscovite	2470	K-Ar	Gast et al. (1958)
Muscovite	2800	Rb-Sr	Gast et al. (1958)
Microcline	2700	Rb-Sr	Gast et al. (1958)

Table 18. (Continued)

Sample Number and Mineral	K %	<u>New Data</u>		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
AWL-6-67, Muscovite	8.66 ± 0.05 8.65 ± 0.06	806.4	0.2	2500 $\pm$ 80	--
AWL-10-67, Albite	0.44 ± 0.02 0.43 ± 0.01	43.99	1.3	2610 $\pm$ 80	3.46*
AWL-8-67, Quartz	0.014 $\pm$ 0.001 0.013 $\pm$ 0.001	7.424	2.9	--	6.167*

*With respect to muscovite K-Ar age.

The albite from the pegmatite shows no excess ^{40}Ar if the reference age is correct. The two low muscovite ages may indicate some post-emplacement thermal perturbation but this cannot be substantiated without additional geochronological studies. The albite does show argon retention higher than that of the muscovite.

Bob Ingersoll Mine, Keystone, South Dakota

The Bob Ingersoll mine is one of the major pegmatite producers in the Keystone district of the Black Hills pegmatite area. In actuality the mine consists of five pegmatites, two of which have been extensively mined. The mine is located about two miles northwest of Keystone, Pennington County in the NE $\frac{1}{4}$, NW $\frac{1}{4}$, sec. 6, T. 2 S., R. 6 E.

A brief summary of the geology of the deposits is taken from the work of Weis (1953) and Hanley (1953).

The pegmatites are zoned, complex, lithium-rich bodies enclosed by Precambrian country rock. The wall rocks are schists, amphibolites, and quartzites; with garnet, staurolite and sillimanite schists predominating. Contacts with the wall rocks are sharp and irregular. The schists are commonly crumpled near the contacts and a tourmalinized zone one to six inches wide may be present.

Both of the major pegmatites are well zoned. Dike No. 1 has six zones ranging from a quartz-clevelandite-muscovite border zone through a series of discontinuous

intermediate zones to a core of quartz-clevelandite-lepidolite. Dike No. 2 has seven zones ranging from a fine grained border zone of quartz-albite-muscovite again through discontinuous intermediate zones to a quartz-spodumene core.

The pegmatites of the Black Hills including those of the Bob Ingersoll mine lie on the flanks of the Harney Peak granite and most of them dip away from the granite. Page et al. (1953) consider that "the Black Hills pegmatites were formed from solutions derived from the differentiation of the Harney Peak granite." They believe that the pegmatites were emplaced with sufficient pressure to deform the wall rocks and yield gneissic structures in some of the pegmatites. Fractional crystallization in situ was considered to be the dominant process in the formation of the zoning, replacement processes being of minor importance.

Prior Geochronological Work

The Bob Ingersoll Mine (Pit or Dike No. 1) is probably one of the best dated pegmatites in the world and as may be seen from Table 19, several methods have been applied to the dating of a variety of minerals from this pegmatite. The results range from a low of 1090 ± 50 m.y. on microcline by the K-Ar method to a high of 1730 ± 80 m.y. on muscovite by the Rb-Sr method. Most of the results fall in the range from 1550 m.y. to 1650 m.y. The low microcline

Table 19. Bob Ingersoll Mine (Pit No. 1), Keystone,
South Dakota.

Mineral	Method	<u>Reference Ages</u>	
		Age m.y.	Reference
Uraninite	Pb ²⁰⁶ /U ²³⁸	1580±30	Wetherill et al. (1956)
	Pb ²⁰⁷ /U ²²⁵	1600±20	Wetherill et al. (1956)
	Pb ²⁰⁷ /Pb ²⁰⁶	1630±30	Wetherill et al. (1956)
	Pb ²⁰⁸ /Th ²³²	1440±75	Wetherill et al. (1956)
Lepidolite	K-Ar	1380±60	Wetherill et al. (1956)
	Rb-Sr	1690±80	Wetherill et al. (1956)
	Rb-Sr	1540	Davis and Aldridge (1953)
	Rb-Sr	1660±80	Wetherill et al. (1956)
	Rb-Sr	1650±80	Wetherill et al. (1956)
Muscovite	K-Ar	1550±60	Wetherill et al. (1956)
	Rb-Sr	1730±80	Wetherill et al. (1956)

Table 19. (Continued)

Mineral	Method	<u>Reference Ages</u>	
		Age m.y.	Reference
Microcline	Rb-Sr	1600±120	Wetherill et al. (1956)
	K-Ar	1090±50	Wetherill et al. (1956)
Lepidolite	Rb-Sr	1576	Herzog (1956)
Lepidolite	Rb-Sr	1620	Giletti and Gast (1961)

age may be disregarded as the potassium feldspars are noted for yielding low ages. Recent work by Riley (1967, personal communication) indicates Rb-Sr ages on muscovites ranging from 1640 to 1740 m.y. and on lepidolites grouping at 1680-1700 m.y. From available data a mean age of about 1590 ± 90 m.y. could be taken as the best approximation of the time of emplacement of this pegmatite.

Analytical Results and Discussion

Three samples from the Bob Ingersoll mine were analyzed during this study. The results of these analyses are given in Table 20. A coarse muscovite crystal was analyzed for comparison with the results of other workers.

Table 20. Bob Ingersoll pegmatite, Keystone, South Dakota.

Sample Number and Mineral	K %	New Data		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
AWL-3-66m, Muscovite	8.29 ± 0.07 8.29 ± 0.04	374.3	0.7	1610 $\pm$ 50	--
AWL-3-66a, Albite	0.107 $\pm$ 0.005 0.106 $\pm$ 0.003	44.85	0.8	4900 $\pm$ 150	40.04
AWL-28-66, Beryl	0.048 $\pm$ 0.001 0.048 $\pm$ 0.001	79.31	2.2	--	76.43

This sample gave an apparent age of 1610 ± 50 m.y. in good agreement with the "best" age assumed above for this pegmatite. To evaluate the excess inert gas age effect a sample of albite was then analyzed. This sample had a potassium content of 0.107% and gave an apparent age of 4900 ± 150 m.y. On the basis of the 1610 m.y. muscovite age, the albite had an excess ^{40}Ar content of 40.0×10^{-10} m/g. This is by far the largest quantity of excess ^{40}Ar recognized in a plagioclase. Because of the high excess ^{40}Ar content of the albite, a sample of beryl was obtained and analyzed. It had a potassium content of 0.048% and contained 76.43×10^{-10} m/g of excess ^{40}Ar . This value is slightly lower than the mode of Damon and Kulp's (1958) histogram for Precambrian beryls less than 2300 m.y. old. The ratio of excess ^{40}Ar in beryl to that in albite is about two, in sharp contrast to the ratio in the Rutherford and Beryl Mountain pegmatites.

Pegmatite, Governador Valadares,
Minas Gerais, Brazil

An albite-muscovite pair was analyzed from a pegmatite from Governador Valadares, Minas Gerais, Brazil. No geological or prior geochronological data was available for this pegmatite. Both minerals were separated from an extremely vuggy sample of large muscovite crystals, albite, and minor pyrite and rutile.

Analytical Results and Discussion

The analytical results on these samples are given in Table 21. The reference age for this pegmatite was obtained from the muscovite K-Ar age of 493 ± 15 m.y. The cogenetic albite had a potassium content of 0.025% and gave an apparent age of 1120 ± 70 m.y. This anomalous age may be accounted for by the incorporation of 0.43×10^{-10} m/g of excess ^{40}Ar .

Canoa Ranch Pegmatite, Arizona

The Canoa Ranch pegmatite is located on the eastern flank of the Sierrita Mountains south of Tucson and is related to a major Laramide pluton. The geochronology of the pegmatite and the pluton has been discussed by Livingston et al. (1967) and is summarized in Table 22. Potassium-argon results on a muscovite from the pegmatite yield an age of 50.7 m.y. The Rb-Sr age of the muscovite is 40 ± 8 m.y. Livingston et al. reported an excess ^{40}Ar content of 0.14×10^{-10} m/g for albite from this pegmatite.

A sample of quartz from the pegmatite was analyzed to allow comparison of the excess argon contents of quartz and albite. Low level beta counting of this sample indicated a potassium content of about 0.01%; the argon content was 0.6695×10^{-10} m/g. Assuming an age of 50.7 m.y. the excess ^{40}Ar content was 0.580×10^{-10} m/g, about four times that of the albite.

Table 21. Pegmatite, Governador Valadares, Minas Gerais, Brazil.

Sample Number and Mineral	K %	<u>New Data</u>		Apparent Age m.y.	Apparent Excess ^{40}Ar $\times 10^{-10}\text{m/g}$
		^{40}Ar radiogenic $\times 10^{-10}\text{m/g}$	^{40}Ar atmos. %		
AWL-1-66m, Muscovite	8.58 ± 0.06	86.19	2.3	493 ± 15	--
	8.62 ± 0.06				
AWL-1-66a, Albite	0.025 ± 0.001	0.681	24.0	1120 ± 70	0.430
	0.025 ± 0.001				

Table 22. Canoa Ranch pegmatite.

<u>Reference Ages</u>					
Mineral	Age m.y.	Method	Reference		
Muscovite	50.7	K-Ar	Livingston et al. (1967)		
Muscovite	40	Rb-Sr	Livingston et al. (1967)		
<u>Previously Reported Excess ⁴⁰Ar</u>					
Mineral	Apparent Excess ⁴⁰ Ar x 10 ⁻¹⁰ m/g	Reference			
Albite	0.14	Livingston et al. (1967)			
<u>New Data</u>					
Sample Number and Mineral	K %	⁴⁰ Ar radiogenic x 10 ⁻¹⁰ m/g	⁴⁰ Ar atmos. %	Apparent Age m.y.	Apparent Excess ⁴⁰ Ar x 10 ⁻¹⁰ m/g
AWL-5-66, Quartz	0.01*	0.670	46.1	2070±60	0.580

*Low level beta counting.

Excess ^{40}Ar in Albites from other Pegmatites

Excess ^{40}Ar has been reported in albite from one pegmatite not examined during this study. Damon and Kulp (1958) reported ages on albites from the Beryl Mountain, New Hampshire pegmatite that exceeded the age of cogenetic muscovite. These ages have been interpreted by Livingston et al. (1967) as resulting from the incorporation of about 0.6×10^{-10} m/g of excess ^{40}Ar .

The Excess Inert Gas Age Effect in Pegmatitic Plagioclases

Cogenetic plagioclase-mica pairs have been analyzed from 12 pegmatites, 10 of which were analyzed during this study. Eight of the 12 pegmatites contain plagioclases that yield older ages than do the cogenetic micas. In one of these, however, while the plagioclase is older than the muscovite, it is younger than the ages obtained by the Rb-Sr and model Pb methods. Plagioclases from the other four pegmatites gave ages distinctly younger than the mica ages. One of the pegmatites yielding a young plagioclase age was known to have been reheated during the deposition of Laramide or mid-Tertiary volcanics.

In Figure 16 the plagioclase ages have been plotted versus the assumed true age of the pegmatites. A perfect chronometer line representing complete retention of radiogenic ^{40}Ar and no incorporation of excess ^{40}Ar has been

Figure 16. Perfect Chronometer Plot of Plagioclase from Intrusive Rocks

drawn in for reference purposes. From this figure it is possible to assess the existence of the excess inert gas age effect in plagioclases. If the quantity of excess ^{40}Ar incorporated by the plagioclases remained relatively constant throughout geologic time then a line through the points should, with increasing true age, become asymptotic to the perfect chronometer line. On the other hand if the age effect observed by Damon and Kulp (1958) in the cyclosilicates is also present in plagioclases then a line through the points should not become asymptotic to the perfect chronometer line. Although the picture is somewhat clouded by samples showing argon loss, there appears to be no tendency for the differences between the plagioclase and true ages to decrease with increasing sample age. It is apparent that an age effect does exist in plagioclase, although on a lesser scale than in the cyclosilicates.

Let us now consider the possible causes of such an age effect. Damon and Kulp (1958) have proposed two causative mechanisms: (1) higher argon pressures at the time of crystallization of older samples because of higher heat production in the past resulting in a greater rate of lithospheric degassing and (2) diffusion into the minerals occurring progressively with time. After a thorough discussion of the two mechanisms they concluded that the first was more

probable. They felt that low temperature diffusion processes had disadvantages which outweighed the time dependence.

This study has not yielded definitive proof supporting either theory. As will be demonstrated later in Chapter VII significant quantities of argon may be introduced into albite even at argon pressures as low as one bar. This observation when combined with recognition of the large low-temperature argon loss from the potassium feldspars suggests that some redistribution of argon may occur during periods of low temperature heating. High potassium minerals such as the potassium feldspars would tend to act as sources for the ^{40}Ar while the low potassium minerals would tend to act as sinks or receivers of the ^{40}Ar . Older rocks would have a higher probability of being reheated either due to igneous or metamorphic activity or simply because of deep burial. Thus we might expect larger quantities of excess ^{40}Ar to be present in the older minerals.

The gradual increase of excess ^{40}Ar during crystallization as was shown by the albites from the Rutherford pegmatite suggests, however, that the differences are related to actual differences in the partial pressure of ^{40}Ar at the time of crystallization and not to later introductions of ^{40}Ar . Additional studies of minerals with a known paragenesis are necessary to determine if these changes are significant or are only fortuitous.

CHAPTER VI

HEATING EXPERIMENTS AND THEIR RELATION TO THE LOCATION OF EXCESS ^{40}Ar

It is reasonable to suppose that radiogenic, excess and inherited argon might occupy different positions in a mineral. The radiogenic argon is, of course, generated in a potassium site in the crystal lattice and should remain in that site, excepting later migration. Since inherited argon is simply radiogenic argon that escaped loss during metamorphism, it should also occupy a potassium site unless migration occurred during metamorphism. In contrast, a variety of sites have been suggested for the location of excess argon. Damon and Kulp (1958) suggested that in the cyclosilicates the excess argon was contained in the tubular channels characteristic of these minerals. Fluid inclusions were shown by Gentner (1963), Rama et al. (1965), Naughton et al. (1966), and Funkhouser, Barnes and Naughton (1966) to contain excess argon. Hart and Dodd (1962) suggested that excess argon in pyroxenes was held in dislocations and low angle grain boundaries.

The variety of positions occupied by excess argon suggests that several processes may have operated leading to the incorporation of the argon. This argon may in fact

be considered a trace element and most of the processes leading to the incorporation of a trace element must be considered in evaluating the incorporation of excess argon. McIntire (1963) has pointed out three processes that result in the occurrence of a trace element in a mineral: (1) surface adsorption, (2) occlusion, and (3) solid-solution formation. It is pertinent to discuss these processes and their roles in the incorporation of excess argon by a mineral.

Surface adsorption is the holding of a diffuse layer of foreign ions or atoms by the attraction of surface atoms (McIntire, 1963). Since the amount adsorbed is directly proportional to the surface areas, it is necessary to consider the surface area of the sample to know that amount (see Chapter VIII). This process probably accounts for most of the atmospheric argon held by a mineral. Adsorption also no doubt occurs whenever a mineral crystallizes, the source of the adsorbed argon being the volatiles present in the magma at the time of crystallization. If these volatiles contained argon with a $40/36$ ratio in excess of that of atmospheric argon, as would normally be the case, and if this argon was not removed, an anomalously old age would result. Baking, pumping, and leaching plus ultrasonification have been shown to remove much of the adsorbed atmospheric argon (Evernden and Curtis, 1965) so this phenomena would yield erroneous ages only in the case of very young samples.

Occlusion results from surface adsorbed atoms being trapped during continued growth of the mineral and differs from solid-solution formation because regular positions in the lattice are not occupied. This phenomenon also includes the incorporation of fluid inclusions which as discussed above have been demonstrated to contain excess argon. Indeed it would be amazing if fluid inclusions did not contain excess argon since the aqueous fluid which composes them has some finite solubility for argon. It is important, however, to determine if excess argon is present in any sites besides fluid inclusions. Because the volume occupied by fluid inclusions is small when compared to the total volume of a mineral, the writer intuitively feels that fluid inclusions are a minor source when compared to the other proposed sites of excess argon.

Although argon is of course not a solid and presumably does not occur as an ion, it may occupy an interstitial lattice position or lattice vacancy in a mineral. It may also occupy equilibrium defects which have distributions governed by Arrhenius equations. In such positions the argon concentrations should be governed by a determinable distribution law dependent upon the number of sites and the partial pressure of argon.

Because of the considerable interest in fluid inclusions as a site of excess argon, a series of experiments

was undertaken to determine how much of the excess argon present was located in this site. Two general methods have been employed for releasing argon from fluid inclusions; both having certain advantages and disadvantages. Rama et al. (1965) released argon from fluid inclusions in quartz and fluorite by the decrepitation method, heating the samples to a temperature of 700°C. While this method has the advantage of probably opening most of the inclusions, argon contributions may come from any other site with a low energy of activation. Naughton et al. (1966) employed a vacuum crushing technique to release argon from fluid inclusions. This method may not open all of the inclusions, however, and may cause argon loss from grain boundaries and surfaces. It has been demonstrated by Gerling et al. (1961) for example that grinding of micas causes significant argon loss. After consideration of the relative merits of the two methods the decrepitation method was chosen for these experiments.

Four minerals from the Amelia, Virginia pegmatites were selected for the initial experiments. Three of these, moonstone albite, quartz and topaz were known to contain both fluid inclusions and excess argon. One sample of albite contained excess argon and no visible fluid inclusions and a sample of microcline contained neither fluid inclusions nor excess argon.

The first two samples run were albites, one of which contained many fluid inclusions up to 0.01 mm in length. The second albite contained no fluid inclusions visible with the petrographic microscope. Because of the low temperature of formation of pegmatites it was assumed that a temperature of 770°C would be sufficiently high to cause decrepitation of the inclusions. To minimize diffusional losses the samples were raised to this temperature as rapidly as possible and held there for only one minute. The results of these experiments are shown in Table 23. In both cases a quantity of argon approximately equal to the excess was removed by the heating. After this preliminary heating the samples were rebaked and fused, releasing the remainder of the argon. Since one sample contained no visible inclusions, the results on these two experiments suggest that if fluid inclusions are indeed the source of the excess argon, it must be held largely in inclusions below the limit of detectability of the petrographic microscope.

Additional heating experiments were then made on the samples of quartz, topaz and microcline. The quartz sample was first heated to 770°C for one minute to decrepitate the abundant fluid inclusions. This heating released 0.382×10^{-10} m/g of ^{40}Ar . To determine if any argon was present in sites other than the fluid inclusions, the sample

Table 23.. Heating experiments on Amelia, Virginia pegmatite minerals.

Sample Number	Mineral	Fluid Inclusions	Temp. °C	Time min.	^{40}Ar Loss $\times 10^{-10}\text{m/g}$	^{40}Ar Loss %
AWL-24-65	Moonstone Albite	Abundant	770	1	0.559	35.3
AWL-5-65a	Albite	Rare	770	1	0.357	33.5
AWL-30-65	Quartz	Abundant	770	1	0.382	38.7
			1350	5	0.606	
AWL-26-65	Topaz	Abundant	770	1	0.703	55.3
	Topaz*	Abundant	850-870	52	0.069	5.4
			1200	1	1.27	
AWL-22-65m	Microcline	Very Rare	770	1	13.8	26.8

*Second split of same sample.

was rebaked and heated to a temperature of 1350°C for five minutes. Although fusion was not attained an additional 0.606×10^{-10} m/g of ^{40}Ar was released yielding a total for the sample of 0.988×10^{-10} m/g. Because fusion was not attained some argon was probably retained by the sample. Low-level beta counting was used to determine the potassium content and counting statistics indicate a potassium content of less than 0.03%. Such a potassium content would yield 0.141×10^{-10} m/g of ^{40}Ar during the 248 m.y. age of the sample, leaving 0.847×10^{-10} m/g as the minimum excess ^{40}Ar . If all of the fluid inclusions were broken open by the 770°C heating as seems likely, then a maximum of 45.1% of the excess could be in the fluid inclusion site. This must be considered a maximum value since there was undoubtedly some diffusional contribution to the quantity removed at 770°C. There also was probably some potassium in the fluid inclusions which would have contributed some radiogenic ^{40}Ar to this amount.

Two splits of the topaz which also contained fluid inclusions were next subjected to heating experiments. The first split was heated in two stages with a bakeout between. An initial heating to 770°C for one minute released 0.703×10^{-10} m/g of ^{40}Ar while a second heating to 850-870°C for 52 minutes released only an additional 0.069×10^{-10} m/g of ^{40}Ar . The second split was heated to 1210°C for two

minutes. At that time large quantities of white fumes escaped from the crucible and droplets of a colorless liquid condensed on the walls of the fusion system. Large quantities of fluorine were given off at this point since considerable TiF_4 was formed in the Ti furnace. The 1210°C heating released 1.271×10^{-10} m/g of ^{40}Ar . The heating was not carried to complete fusion because of the corrosive nature of the fluorine compounds released at 1210°C . During the heating of the second split the pressure in the fusion system was monitored with the coarse vacuum gauge. Although the measurements are only qualitative they do show a correlation with the quantities of argon released (Figure 17). The initial large release of argon corresponds to a slight pressure rise up to 800°C while the long pressure plateau from 800° to almost 1000°C is accompanied by release of only 0.069×10^{-10} m/g of ^{40}Ar . The rapid rise in pressure at about 1000°C may be correlated with the loss of 0.568×10^{-10} m/g of ^{40}Ar and the appearance of volatile fluorine compounds. Although some excess ^{40}Ar was released by the preliminary heating, removal of the remainder required the commencement of breakdown of the crystal structure as indicated by the release of fluorine compounds.

The last sample heated in this group was a microcline (AWL-22-65m). This was microcline extracted from the green microcline perthite. The sample before heating had

Figure 17. Fusion System Pressure
During 1220 °C Topaz Heating

an apparent age 8% lower than the cogenetic micas. Upon heating to 770°-790°C for one minute the sample lost 13.80×10^{-10} m/g of ^{40}Ar which represents 26.8% of the total ^{40}Ar .

A first analysis of the results on the two albite samples would seem to indicate that the excess ^{40}Ar is located in some position different from the radiogenic ^{40}Ar and from which it is easily removed at low temperatures. Since one of the albites contained no visible fluid inclusions it is not likely that this site was fluid inclusions. The results on the topaz and quartz also tend to refute the fluid inclusion theory since in both cases all of the excess ^{40}Ar was not removed by the preliminary heating. Both minerals clearly contain some excess ^{40}Ar in sites other than fluid inclusions. The microcline which also contained no visible inclusions and had a deficiency of ^{40}Ar still showed a substantial argon loss during the preliminary heating. The 26.8% loss from the microcline when added to the original 8% loss yields a total of about 35% of the ^{40}Ar which is easily removed from the sample. If we now look at the percentage loss from the albites, a certain pattern develops. In sample AWL-5-65a the preliminary heating released 33.5% of the total ^{40}Ar while AWL-24-65 lost 33.5% under similar conditions. A comparable loss of 38.5% was reported by Amirkhanoff, Brandt and Barnitsky (1961) for a microcline

heated to below 800°C . Amirkhanoff et al. (1961) also demonstrated that in this temperature range the argon loss rapidly becomes independent of heating time which they interpreted as indicating the location of 38.5% of the ^{40}Ar in a low temperature site. This was designated Phase I argon. The data on the albites and the microcline from the Amelia pegmatites substantiate the Russian work and suggests that the phenomena of a large low temperature argon loss may hold true for all feldspars.

The results on the initial experiments raise several questions which must be answered. Is the fact that a quantity of ^{40}Ar , equal to the excess ^{40}Ar contents of the albites, was removed by a 770°C heating fortuitous or do the excess and radiogenic argon occupy different sites? If a constant percentage of argon is released by heating to 770°C , is it a sudden release as might be produced by a phase change or decrepitation of fluid inclusions or is it simply a high diffusional loss caused by a low energy site with a high value of D/r^2 ? To answer these questions, two additional series of experiments were conducted.

It is first necessary to determine if a 770°C heating can be used to distinguish between excess and radiogenic argon. To accomplish this a sample of albite with a very high proportion of excess ^{40}Ar was heated to 770°C for one minute. The sample selected was AWL-4-66a from the

Bob Ingersoll mine, Keystone, South Dakota. This sample originally contained 44.85×10^{-10} m/g of ^{40}Ar , 89.3% of which was excess. The initial heating released 38.6% of the ^{40}Ar (normalized). This agrees well with the results on the other samples and in no way approaches the percentage of excess ^{40}Ar in the sample. It is thus concluded that the quantity of ^{40}Ar removed by the low temperature heating is independent of the relative proportions of excess and radiogenic argon. This conclusion is not in accord with the conclusions of Kistler et al. (1967). From their work on pyroxenes from the Stillwater Complex they concluded that the excess ^{40}Ar was located in a site from which it could be removed at low temperatures and that the true sample age could be obtained from the quantity of ^{40}Ar remaining after this initial heating. It appears strange that in albites the quantity of ^{40}Ar removed by the low temperature heating is unrelated to the quantity of excess ^{40}Ar while in pyroxenes only the excess ^{40}Ar is removed by such heating. Further work is necessary on pyroxenes with varying quantities of excess and radiogenic ^{40}Ar to prove that only the excess ^{40}Ar is removed by low temperature heating.

Several theories may be proposed to explain the large argon losses from feldspars when heated to 770°C . Amirkhanoff et al. (1961) conclude that "(1) The loss of radiogenic gases during geologic time by undisturbed

minerals by means of volume diffusion is impossible. (2) The loss of radiogenic gases occurs by desorption of these gases from boundaries created in the course of various secondary permutations in them. (3) Migration of radiogenic gases in mineral lattices occurs through associated lattice defects accompanying phase transitions." Conclusions (1) and (2) above appear to be somewhat contradictory since volume diffusion is necessary to move the argon to the grain boundary. Presumably phase transitions in feldspars, if they occur in a particular sample, may occur either during initial cooling or during a subsequent thermal event. The percentage of argon available for loss should thus vary greatly between samples. This does not appear to be the case. Experimental evidence and natural observations suggest that roughly one third of the total argon in a feldspar is easily lost.

A second theory is that the loss simply represents volume diffusion from some site with a high value of D/r^2 and/or a relatively low energy of activation. This site would be effectively emptied by the low temperature heating. This theory would agree with the constant percentage loss since it is reasonable to suppose that the different sites in feldspars would contain certain fixed percentages of the total ^{40}Ar .

It is possible to test these theories by measuring the values of argon loss at temperatures below 770°C . These losses can then be used to evaluate D/r^2 at the respective temperatures. The optical pyrometer used for temperature measurements during sample fusions can not measure temperatures below 770°C . As an alternative method, a small Kanthal furnace was constructed in which a thermocouple and a pyrex tube containing the sample could be placed. The end of the pyrex tube was left open and the argon released was allowed to escape into the atmosphere. The sample used was the microcline (AWL-22-65m) used in the one minute heating experiments. Splits of this sample were heated to increasingly high temperatures for varying periods of time. After heating and argon loss the samples were fused and the quantity of argon remaining in the sample measured. The results of these experiments are shown in Table 24.

The argon losses at the different temperatures were used to evaluate D/r^2 from equations 4a and 4b of Fechtig and Kalbitzer (1966) which assume a spherical model, a homogeneous distribution of argon at time zero and a zero argon concentration outside the sphere. The calculated values of D/r^2 are given in Table 24 and are plotted as a function of temperature in Figure 18. The values of D/r^2 must be considered apparent values unless it can be demonstrated that only one site was activated over this temperature range.

Table 24. Diffusion losses in microcline (AWL-22-65m).

Run Number	Temp. °C	Time min.	^{40}Ar Loss $\times 10^{-10}\text{m/g}$	^{40}Ar Loss %	Apparent D/r^2 sec.^{-1}
1	375	720	2.54	4.94	4.9×10^{-9}
2	500	70	5.95	11.56	3.0×10^{-7}
3	600	30	7.18	13.95	1.0×10^{-6}
4	675	37	16.41	31.89	4.8×10^{-6}

Let us now evaluate the argon loss from this microcline below 770°C . For the interval $375\text{--}675^\circ\text{C}$ a single straight line fits the experimental data. This indicates that only one site was activated in this temperature range or that contributions from a second site were negligible. It is also apparent that no significant sudden release of argon occurred in this interval for such a release would give a high apparent D/r^2 at the next higher temperature measurement. This would preclude fluid inclusions as a source for the low temperature release (Zero Phase) as was proposed by Rama et al. (1965). It would also preclude any sudden release due to a phase change.

It is of course possible to evaluate the energy of activation (E) of the site from the data presented above. From a best fit line through the four points a value of E of 26 ± 1 kcal/mole can be obtained. Gerling, Levskii and

Figure 18. D/r^2 vs $1/T$ for Microcline AWL-22-65m

Morozova (1963) report for microcline a value of $E = 32$ kcal/mole for the lowest energy site, Evernden et al. (1960) a value of 24 kcal/mole for a single site and Baadsgaard, Lipson and Follinsbee (1961) 18 kcal/mole for a single site. With E known, a value of $(D/r^2)_{600^\circ\text{C}} = 3 \text{ sec.}^{-1}$ was calculated from the relationship $D/r^2 = D_0/r^2 \exp(-E/RT)$. Assuming that D_0/r^2 remains constant with temperature, D/r^2 was extrapolated back to 20°C to obtain a value of $1.4 \times 10^{-19} \text{ sec.}^{-1}$. This sample was passed by a 80 mesh sieve which had openings 0.175 mm in size and was caught on a 150 mesh sieve with openings of 0.104 mm. The mean greatest dimension of the grains would then be about 0.140 mm and the diffusion distance (r) would be less than 0.07 mm. If we assume $r = 0.07 \text{ mm}$ then $D_{20^\circ\text{C}}$ would equal about $7 \times 10^{-24} \text{ cm}^2 \text{ sec.}^{-1}$. This is a maximum value since the true diffusion distance r is certainly less than the physical value of 0.07 mm. This may be compared with a value of $D_{20^\circ\text{C}} = 10^{-26} \text{ cm}^2 \text{ sec.}^{-1}$ reported by Evernden et al. (1960) and $D_{25^\circ\text{C}} = 10^{-20} \text{ cm}^2 \text{ sec.}^{-1}$ reported by Baadsgaard et al. (1961).

The argon losses obtained by heating for one minute at 770°C can be used to place limits on D/r^2 at that temperature. The nature of heating precludes obtaining exact values since a finite period of time was required to raise the sample temperature to 770°C . For example in the case of quartz (AWL-30-65) it required nine minutes to reach

770°C. An upper limit for D/r^2 was calculated from equations 4b and 4c of Fechtig and Kalbitzer (1966) using for time the one minute at 770°C. A lower limit was obtained by using for time the total heating time. The results of these calculations are given in Table 25.

Table 25. Apparent D/r^2 for one minute heating at 770°C.

Sample Number	Mineral	Maximum Apparent D/r^2 $\times 10^{-3} \text{ sec.}^{-1}$	Minimum Apparent D/r^2 $\times 10^{-4} \text{ sec.}^{-1}$
AWL-24-65	Albite	2.5	3.1
AWL-5-65a	Albite	2.0	2.5
AWL-4-66a	Albite	3.9	4.9
AWL-22-65m	Microcline	1.0	1.3
AWL-30-65	Quartz	4.0	5.0
AWL-26-65	Topaz	3.2	4.0

Because of the large total quantity of argon in the albite from the Bob Ingersoll mine, additional heating experiments were continued after the initial one minute 770°C heating. The results of these experiments are given in Table 26 and Figure 19. To confirm the conclusion of Amirkhanoff et al. (1961) that argon loss rapidly becomes independent of time at low temperatures, the sample was heated an additional 30 minutes at 770°C. This heating released only 3.4% of the total ^{40}Ar . The sample temperature was next raised to 900°C and held at that temperature

Table 26. Heating results on albite (AWL-4-66a).

Time min.	Temperature °C	^{40}Ar Loss $\times 10^{-10}\text{m/g}$	^{40}Ar Loss cor. $\times 10^{-10}\text{m/g}$	Fraction ^{40}Ar Removed	Fraction ^{40}Ar Remaining
1	770	16.35	17.29	0.385	0.615
30	770	1.46	1.54	0.034	0.581
1	900	0.0	0.0	0.000	0.581
1	975	0.40	0.42	0.009	0.572
1	1050	2.34	2.47	0.055	0.517
30	1050	17.07	18.06	0.403	0.215
15	1050	1.48	1.57	0.035	0.152
	<u>Fusion</u>	<u>3.31</u>	3.50	0.078	0.0
	Total	42.41			

Original ^{40}Ar content - $44.85 \times 10^{-10}\text{m/g}$

Total from above - $42.41 \times 10^{-10}\text{m/g}$

Difference - $2.44 \times 10^{-10}\text{m/g} = 5.44\%$

Figure 19. Fraction ^{40}Ar Remaining in
AWL-4-66a After Heating

for one minute, no detectable argon being released. One minute heating at 975°C released only 0.9% of the total ^{40}Ar . The temperature of the sample was next raised to 1050°C and held there one minute, releasing 5.5% of the ^{40}Ar . Thirty minutes additional heating at that temperature released 40.3% and 15 minutes additional 3.5%. Fusion of the sample released the remaining 7.8%. Since the total removed during the eight runs differed by 5.44% from the total removed in the initial run, the individual runs were corrected accordingly.

The fraction of argon remaining in AWL-4-66a is plotted in Figure 19 as a function of temperature and time. As discussed above, after the initial large loss at 770°C there is little additional loss until 1050°C is reached. The fraction lost at 770°C appears to decrease with time as suggested by Amirkhanoff et al. (1961) and may indicate the almost complete removal of argon from some site with a low energy of activation and a high D/r^2 . At 1050°C however, the loss does not appear to level out but continues rapidly toward complete removal of the remaining argon.

Figure 19 clearly shows that the ^{40}Ar in this albite is located in more than one site. The low temperature site, effectively emptied at 770°C , contains about 43% of the ^{40}Ar in the albite. The shape of the curve in Figure 19 strongly suggests that only one other site was present in this sample.

Values of D/r^2 may be calculated for the diffusion from the two sites in this sample. For the low temperature site, equation 4b of Fechtig and Kalbitzer (1966) was used to place upper and lower limits on D/r^2 at 770°C . The maximum D/r^2 at this temperature is $3.9 \times 10^{-3} \text{ sec.}^{-1}$ and the minimum is $4.9 \times 10^{-4} \text{ sec.}^{-1}$. At 1050°C the method of Damon (1968) was used to calculate D/r^2 . This method, assuming a spherical model, gives a value of $1.5 \times 10^{-5} \text{ sec.}^{-1}$. Insufficient data were available to calculate the energy of activation.

The heating experiments on natural samples furnish considerable evidence on the behavior of argon in a mineral. First, the conclusion of Amirkhanoff et al. (1961) that ^{40}Ar is located in more than one site in potassium feldspars is substantiated. This conclusion also apparently holds true for albite. Secondly, although the ^{40}Ar is present in multiple sites, it is operationally impossible to distinguish between excess and radiogenic ^{40}Ar by heating experiments. The feldspars apparently contain a roughly constant percentage of their total ^{40}Ar in a low temperature site irrespective of the relative proportions of excess and radiogenic ^{40}Ar . In microcline this low temperature site is activated by an energy of $26 \pm 1 \text{ kcal/mole}$. Thirdly, the release of the low temperature ^{40}Ar component is not sudden but follows the relationship $D/r^2 - D_0/r^2 \exp(-E/RT)$. Thus

it is not likely that fluid inclusions or phase transitions produce the loss. Fourthly, since excess ^{40}Ar is present in minerals with and without fluid inclusions and because all of the excess ^{40}Ar is not removed by heating to temperatures above that necessary to decrepitate fluid inclusions, it is unlikely that the inclusions are a major source of the excess ^{40}Ar in these albites.

CHAPTER VII

ARTIFICIAL INTRODUCTION OF ARGON INTO ALBITE

It has been demonstrated that an age effect exists in the quantity of excess ^{40}Ar incorporated by pegmatitic albites. Recognizing the existence of such an effect, it is pertinent to ask if there is some saturation value for the quantity of excess ^{40}Ar in albites. In an attempt to answer this question Dr. Hatten S. Yoder, Jr. of the Geophysical Laboratory, Carnegie Institution of Washington kindly offered to subject albite samples to varying pressures of argon while at high temperatures. It was hoped that, in addition to determining if there is a maximum value of argon that can be held in the albite structure, this part of the investigation would reveal a simple relationship between the argon pressure at the time of crystallization and the quantity of excess ^{40}Ar incorporated.

Several Russian workers have performed argon introduction experiments on a variety of minerals. The most thorough of these was by Gerling et al. (1965). In their experiments samples of pyroxene, amphibole, biotite, olivine, albite and beryl were subjected to argon pressures

of 100 bars. Table 27 is reproduced from their work with conversion of the quantities of argon to moles/gram.

In additional experiments on pyroxene Gerling and his co-workers proved that the quantity of argon incorporated within a mineral increases with both temperature and argon pressure and that saturation at a particular high temperature and pressure is achieved very rapidly (less than one hour). A conclusion that intuitively seems unlikely may be drawn from the Russian data. These data appears to indicate that the type of structure of the mineral has little influence on the quantity of argon incorporated. A variety of crystal structures are represented in the minerals used in these experiments. Pyroxene and amphibole are inosilicates, biotite is a phyllosilicate, olivine is a nesosilicate, albite is a tectosilicate, and beryl is a cyclosilicate. Despite the great differences in structures the amount of argon introduced varied by only one order of magnitude.

Karpinskaya, Ostrovskii and Shanin (1961) conducted similar experiments on muscovite. Working at different pressures, temperatures and times they were able to introduce up to about 4×10^{-6} m/g of argon into this mineral.

Another experiment bearing on this problem was performed by Schreyer, Yoder and Aldrich (1960). These workers subjected a crystalline cordierite to an argon pressure of

Table 27. Quantity of argon introduced under 100 bars pressure,

Mineral	T °C	Amount of Absorbed Ar $\times 10^{-6}$ m/g	Initial Amount of Ar $\times 10^{-10}$ m/g
Pyroxene	1050	0.263	8.70
Amphibole	1000	2.14	25.7
Biotite	1000	2.57	268
Olivine	1000	0.678	0.446
Albite	1050	0.567	223
Beryl	1050	1.64	2230
Amphibole	550	0.232	156

10 kbars at 900°C for five hours. Subsequent analysis showed that 2-3 weight percent argon corresponding to roughly $5-7.5 \times 10^{-4}$ m/g was incorporated by the cordierite.

The Canoa Ranch albite (RM-9-63) was selected for the incorporation experiments which were performed by Dr. Yoder. This is a low-albite with a potassium content of 0.09%. Before any introduction the sample contained 0.225×10^{-10} m/g of ^{40}Ar . A plus 100 mesh split of this sample was used. All samples were held at $1000^\circ\text{C} \pm 50^\circ$. Times and pressures were varied during the several experiments. Argon pressures varied from 1 bar to 10 kbars. Following completion of each argon introduction experiment, the

samples were quenched and sent to the writer for analysis. The samples were fused and analyzed in the standard manner in use at this laboratory with the exception of the sample used for diffusion experiments. Since Dr. Yoder used atmospheric argon for introduction, extreme care was taken to insure that there were no leaks in the fusion system during the runs. The mass spectrometer was used as a leak detector before all of the analyses.

The results of the argon introduction experiments are shown in Table 28. Run 1 under 10 kbars argon pressure introduced 3.15×10^{-6} m/g of argon into the sample. Runs 2a and 2b were splits taken from one sample held at 2 kbars pressure. Run 2a was analyzed upon receipt while Run 2b was made eight months later to determine if any argon had leaked from the sample. As may be seen from the table, the results on the 2 kbars samples are clearly anomalous, being far outside experimental error. Both runs had similar sensitivities (moles $^{38}\text{Ar}/\text{mv.}$) indicating no loss of ^{38}Ar from the spikes. Sample weights were double checked and the system carefully leak checked before analysis so these factors may be eliminated as a source of error. The most plausible source of error is sample inhomogeneity. Weighting the quantities removed according to sample weight results in a total for 2 kbars of 5.05×10^{-6} m/g.

Table 28. Introduction of argon into albite.

Run Number	Time Hours	Temperature °C	Argon Pressure bars	^{40}Ar Introduced $\times 10^{-6}\text{m/g}$
1	24	1000 $\pm$ 50	10,000	3.15
2a	24	1000 $\pm$ 50	2,000	4.20
2b	24	1000 $\pm$ 50	2,000	6.34
3	24	1000 $\pm$ 50	185	0.685
4	24	1000 $\pm$ 50	1	0.00278
5	168	1000 $\pm$ 50	1	0.00407
6	338	1000 $\pm$ 50	1	0.00266*
7	338	1000 $\pm$ 50	1	0.0101

*Pressure decreased to 0.01 for last 2-3 hours.

The sample used in Run 3 was held under an argon pressure of 185 bars. This sample was heated to various temperatures for extended periods of time to obtain data for the calculation of diffusion coefficients (Table 29). At this point in the account only the total quantity of argon introduced in the sample ($0.685 \times 10^{-6} \text{ m/g}$) is of interest.

The samples used for Runs 4, 5, 6 and 7 were treated in a slightly different manner. Instead of being placed in a bomb under a high argon pressure, the samples were placed in tubes with a continuous stream of argon passing over

them. Sample 4 was held at 1000°C in this argon stream for 24 hours while sample 5 was so held for 168 hours. Sample 4 contained 2.78×10^{-9} m/g of argon after introduction. After 168 hours in the argon stream, sample 5 contained 4.07×10^{-9} m/g of argon, an increase of 46.2% over the quantity introduced in 24 hours. Only in Runs 4, 5, 6 and 7 was the original atmospheric argon content a significant fraction (about 1%) of the total argon introduced. Consequently these runs were corrected by the maximum quantity of atmospheric argon measured in the two analyses of RM-9-63 before argon introduction.

Since apparently saturation is not attained rapidly at one bar pressure, the one bar introduction was continued for two weeks. During Run 6 the argon tank was emptied shortly before the experiment was concluded and while the temperature was still at 1000°C. Normal air thus replaced the one bar of argon over the sample. In effect the sample was submitted to a drop of argon partial pressure from one bar to 0.01 bar for about 2-3 hours while at 1000°C. When analyzed the sample contained 2.66×10^{-9} m/g of argon, slightly less than the quantity incorporated in 24 hours. This experiment was repeated yielding a result of 10.1×10^{-9} m/g as the quantity introduced in two weeks at one bar and 1000°C. The brief period at a reduced argon partial pressure caused an argon loss of about 73.7%.

This accident during the two week run was actually useful since it closely duplicated the pressure changes to be expected during extrusion of lava at the earth's surface. After extrusion lava would be exposed to an argon partial pressure of about 0.01 bar. This pressure is, of course, insufficient to retain the argon incorporated within the minerals during crystallization at higher argon pressures. Large scale diffusional losses will occur and only in the case of large phenocrysts is it likely that argon will be retained. This is an experimental demonstration of the conclusions reached by Damon et al. (1967) based upon measurements of minerals from volcanic rocks.

The experimental data may be used to evaluate the saturation concentration (S^*) of argon in albite by means of the following equation from Jost (1960):

$$S = \frac{S^* b_p}{1 + b_p} \quad \begin{array}{l} \text{Where } S = \text{solubility of argon} \\ p = \text{partial pressure of argon} \\ b = c \exp (-E/kt) \end{array}$$

At low values of b_p this equation reduces to Henry's law while at high pressure $S = S^*$. Using the results from the 185 bars and 2 kbars runs, values of $b = 2.7 \times 10^{-4}$ bars⁻¹ and $S^* = 1.44 \times 10^{-5}$ m/g were calculated. These values would predict a value of $S = 0.389 \times 10^{-8}$ m/g at 1 bar.

The quantities of argon introduced at 1 bar are of particular interest since they closely approximate

quantities of excess argon reported in natural albites. Albite from the Bob Ingersoll pegmatite, for example, contained 4.0×10^{-9} m/g of excess ^{40}Ar . The above experiments suggest that the argon partial pressure prevailing in the Bob Ingersoll pegmatite at the time of the crystallization of the albite must have been approximately 1 bar.

Diffusion Experiments on Albite
with Introduced Argon

Diffusion experiments on natural albites and microcline indicated that the argon was held in multiple sites. A series of similar experiments were conducted on the albite containing argon introduced under 185 bars pressure. The results of these experiments are shown in Table 29 and Figure 20. During the experiments the temperature was raised as rapidly as possible with the usual induction heating coil. The fusion system was baked and leak checked between each of the runs.

It is of particular interest to note the differences in the fraction of argon removed from the artificially introduced sample by heating to 770°C for one minute and the fraction removed from natural samples under the same conditions. In the natural samples roughly one third of the total argon was removed; the sample containing artificially introduced argon lost less than 2% during a similar treatment.

Table 29. Removal of argon from RM-9-63 albite after introduction under 185 bars argon pressure.

Run Number	T °C	Time Min.	Cum. Time Min.	^{40}Ar Removed $\times 10^{-8}\text{m/g}$	Fraction ^{40}Ar Remaining
1	770	1	1	1.289	0.9812
2	770	10	11	1.304	0.9622
3	770	30	41	1.806	0.9359
4	770	50	91	1.456	0.9147
5	920	1	92	1.637	0.8908
6	920	10	102	4.998	0.8179
7	920	30	132	1.995	0.7888
8	920	50	182	1.691	0.7641
9	1050	1	183	14.51	0.5524
10	1050	10	193	29.48	0.1223
11	1050	30	223	4.821	0.0520
12	Fusion			3.555	0.0000
Total ^{40}Ar Removed				$68.542 \times 10^{-8}\text{m/g}$

Figure 20. Fraction ^{40}Ar Remaining in RM-9-63 (185 bars)

Significant loss of argon did not take place in the artificially treated sample until 1050°C was reached. Heating to this temperature for one minute produced an argon loss of about 21.2% while an additional 10 minutes of heating at this temperature removed 43.0% more of the argon.

Before further discussion of the results of these experiments it is pertinent to review the expected results of diffusion of argon from one site in a mineral. Jost (1960) gives the equation for the fraction (r) remaining in a slab as:

$$r = \frac{\bar{c}}{c_0} = \frac{1}{h} \int_0^h (c/c_0) dx = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-[2n+1]^2 y)$$

$$\text{where } y = \frac{D \pi^2 t}{h^2} \quad \text{and } D = \text{diffusion coefficient}$$

$$h = \text{diffusion distance}$$

Using calculated values of r from Jost (1960), Figure 21 was prepared. This figure shows the quantity of argon remaining in the slab after heating for two values of D/h^2 . Because of uncertainties in the values of the diffusion distance, D/h^2 was used in place of D. It is readily apparent that as time becomes long, the relative loss becomes exponential. For short periods of time, however, the losses are not exponential and when plotted against time would appear to indicate diffusion from multiple sites.

Figure 21. Fraction Argon Remaining in a Slab
According to Equation of Jost (1960)

The results obtained from heating RM-9-63 for varying periods of time at 770°C closely resemble the theoretical curve in Figure 21. To obtain greater precision in the estimation of D/h^2 the results have been replotted as $(1-r)$ versus time. An approximation of $D/h^2 = 0.2 \times 10^{-6} \text{ sec.}^{-1}$ was obtained from the straight line portion of the 770°C curve in Figure 22. The method of successive approximations was then used to obtain the best fit to the experimental curve. A value of D/h^2 of $0.3 \times 10^{-6} \text{ sec.}^{-1}$ yields points closely fitting the curve. The maximum uncertainty on this value would be approximately $0.1 \times 10^{-6} \text{ sec.}^{-1}$. The small differences between the experimental and theoretical curves at small values of t are probably caused by the finite period of time required to bring the sample to a temperature of 770°C. At small values of t this period of time is significant.

The data collected at 920°C have been treated in a similar fashion. Fractional losses were calculated from the quantity of argon remaining in the sample after heating at 770°C and these values were plotted against time. This is of course not completely justified since concentrations gradients were set up in the sample by the 770°C heating. It is apparent from Figure 23 that no single value of D/h^2 will yield the experimental curve. The sharp knee in this curve indicates that diffusion is occurring from more than

Figure 22. Fractional ^{40}Ar Loss
from RM-9-63 at 770 °C

Figure 23. Fractional ^{40}Ar Loss from RM-9-63 at 920 °C

one site in the albite. As discussed below, resolution of this curve is more difficult than that for 770°C but values of D/h^2 of about 0.3×10^{-5} and 0.04×10^{-5} appear to best fit the curve. The shape of the curve also indicates that the site having the larger diffusion coefficient has been effectively emptied while heating at 920°C. This site which is apparently emptied will for the sake of simplification be referred to as site A. If the reasonable assumption is made that site A is the site having a D/h^2 of 0.3×10^{-6} at 770°C, then values may be obtained for the energy of activation (E) of this site and for $(D/h^2)_{200^\circ\text{C}}$ since $(D/h^2)_T = D_0/h^2 \exp(-E/RT)$. A value for E of about 38 kcal/mole and a value for $(D/h^2)_{200^\circ\text{C}}$ of $1 \times 10^{-27} \text{ sec.}^{-1}$ were obtained from these calculations. The value for E may be compared with the values for Phase I argon in microcline of 33 kcal/mole (Amirkhanoff et al., 1961) and 32 kcal/mole (Gerling et al., 1963). Fechtig, Gentner and Zahringer (1960) determined a single value of E of 56 kcal/mole for anorthite and a value for $D_{200^\circ\text{C}}$ of $10^{-30} \text{ cm}^2 \text{ sec.}^{-1}$. Values of $(D/h^2)_{200^\circ\text{C}}$ as quoted in Fechtig and Kalbitzer (1966) for sanidines vary from 4×10^{-28} to $3 \times 10^{-33} \text{ sec.}^{-1}$.

To obtain the best fit to the 920°C experimental curve, using values of D/h^2 from the straight line portions of the curve, it is necessary to assume that 6% of the argon, present at the beginning of 920°C heating, is located in

site A. When this quantity is added to the quantity removed during the 770°C heating a value for site A of 14% of the total argon is obtained. The remainder of the argon is located in one or more additional sites.

Results from the 1050°C heating have been treated similarly. The quantity of argon remaining after the 920°C heating was used to calculate fractional losses at 1050°C. These losses have been plotted against time in Figure 24. A value of D/h^2 of $4 \times 10^{-4} \text{ sec.}^{-1}$ yields a close fit to the straight line portion. Curvature of the line in the region above 0.75 loss may indicate either activation of a third site or an asymptotic approach to complete argon loss. Unfortunately the experiment was not carried on sufficiently long to distinguish between these alternatives.

Because of the uncertainties in the number of sites and the corresponding values of D/h^2 , no attempt was made to calculate values of the energy of activation for other than the lowest energy site.

Figure 24. Fractional ^{40}Ar Loss from
RM - 963 at 1050 °C

CHAPTER VIII

ATMOSPHERIC ^{40}Ar AND THE SURFACE AREA OF MINERALS

In Chapter VI surface adsorption was discussed as a mechanism for the incorporation of atmospheric ^{40}Ar by a sample. Since the precision of an argon determination depends primarily upon the percentage of atmospheric ^{40}Ar in the sample, the quantity of adsorbed argon becomes critical in young samples. Although, as Damon et al. (1967) have pointed out, the quantity of excess ^{40}Ar is probably the ultimate limiting factor in the dating of young samples, the absolute quantity of atmospheric ^{40}Ar is also highly critical.

Various techniques are in use to remove this adsorbed ^{40}Ar , including acid washes, ultra-sonification, vacuum baking and sample preparation in an argon-free atmosphere. In spite of the awareness of the significance of the problem and attempts to remove the atmospheric component, there have been few attempts to correlate the quantity of adsorbed argon with mineral type or structure. McDougall (1966) has published a table showing the absolute quantities of atmospheric argon held by various mineral and whole rock samples. This table is reproduced

as Table 30 with conversion of the quantities to moles/gram. Similar values were measured for the samples used in this study and these results are included in the same table. Agreement for the same mineral between the two sets of data is good.

Table 30. Absolute quantities of atmospheric ^{40}Ar .

Mineral	No. of Samples	Mean Atmospheric ^{40}Ar $\times 10^{-10}\text{m/g}$
Whole rock*	31	0.036
Pyroxene*	8	0.24
Sanidine*	5	0.28
Hornblende*	12	0.39
Plagioclase*	12	0.50
Biotite*	32	1.0
Muscovite*	7	2.0
Muscovite**	11	2.2 = 0.4
Albite**	18	0.43 = 0.05
Microcline**	3	0.65 = 0.28
Quartz**	4	0.42 = 0.11
Spodumene**	2	0.17 = 0.06

*McDougall (1966).

**This work.

It is apparent from the table that there are considerable variations in the quantity of atmospheric ^{40}Ar held by different minerals. Muscovite, for example, holds between four and five times as much adsorbed atmospheric ^{40}Ar as do the plagioclases and twice as much as does biotite. The atmospheric argon contents of whole rock samples are about an order of magnitude lower than any of the mineral separates. As pointed out by McDougall (1966) the low atmospheric ^{40}Ar content of the whole rock samples is probably due to the low surface area/gram of sample caused by fusing large (1 cm) fragments.

Because of the predicted relationship between adsorbed argon and surface area, the geometric surface areas were calculated for an albite and a lepidolite. The grain size of the samples chosen were typical of samples used for dating. The albite (AWL-24-65) was -48 + 65 mesh and was assumed to consist of rectangular plates. It was calculated to have a surface area of $90 \text{ cm}^2/\text{g}$. The lepidolite (AWL-27-65L) had a grain size of -42 + 80 mesh and was assumed to consist of rectangular plates with a thickness negligible when compared with the length and width. The lepidolite had a calculated area of $165 \text{ cm}^2/\text{g}$.

Because of the possibility of atmospheric argon entering the micas along the cleavage planes, the effective surface areas of the two samples was measured by the BET

method. In this method it is assumed that an inert gas is adsorbed as a monomolecular layer on the surface of the sample. Measurement of the quantity of gas adsorbed allows calculation of the effective surface area. The lepidolite had a measured area of $5000 \text{ cm}^2/\text{g}$ and the albite an area of $430 \text{ cm}^2/\text{g}$. The lepidolite sample shows a much greater difference between the calculated and measured areas than does the albite. This is probably a reflection of the micaceous structure of the lepidolite with its weak bonds between the sheets. These bonds are easily broken allowing entry of water and other volatiles.

CHAPTER IX

APPLICATIONS OF EXCESS ^{40}Ar TO PETROLOGY

Although this study has proved that pegmatitic albites are unreliable for K-Ar dating it has suggested a possibility that may prove to be of great value in studies of the petrology of pegmatites. The fact that the quantity of excess ^{40}Ar incorporated by a mineral is apparently a function of the partial pressure of ^{40}Ar at the time of crystallization should allow an evaluation of pressure changes in the melt as crystallization proceeds. This record of changes in the partial pressure of ^{40}Ar when combined with the chemical compositions of the minerals crystallizing at a particular point in time should furnish evidence regarding the degree of closure of the system.

In practice such an investigation would require measuring the excess ^{40}Ar contents of several samples of the same mineral crystallizing at different times, for example, samples from the border zone, intermediate zone and core might be analyzed. Since crystallization of large quantities of a hydrous or other volatile-rich mineral would drastically affect the partial pressure of ^{40}Ar , the chemical compositions of the phases crystallizing must also be considered. Neglecting for a moment the effects of

changes in the compositions of the minerals crystallizing, closed system crystallization should be reflected in a steady increase in the excess ^{40}Ar contents with order of crystallization. This rise would result from the gradual decrease in volume available for the volatile phase and thus an increased total pressure. A steady increase followed by a sudden decrease would indicate that the partial pressure of ^{40}Ar had decreased for some reason perhaps because the system opened due to fracturing.

Since crystallization of volatile-rich minerals would increase the mole fraction of ^{40}Ar in the volatile phase it would also increase the partial pressure and hence the excess ^{40}Ar content of a mineral crystallizing at that time. In a zoned pegmatite where the mineralogic composition often changes greatly between zones, this might lead to abrupt changes in the excess ^{40}Ar contents. Although it would probably not be possible to treat the data quantitatively, qualitative estimates of the partial pressure changes should be possible.

In Figure 25 changes in the excess ^{40}Ar contents of a single mineral species have been traced through the crystallization of a hypothetical pegmatite. From point a to b continued crystallization of a single mineral assemblage under closed system conditions is reflected in the steady increase in the excess ^{40}Ar contents. At point b a new

Figure 25. Changes in the Excess ^{40}Ar Contents of a Single Mineral Species During Crystallization of a Hypothetical Pegmatite

volatile-rich phase begins to crystallize; leading to a steepening in the slope of the line. When point c is reached, fracturing occurs and the ^{40}Ar partial pressure decreases rapidly to essentially zero.

The ideas discussed above are amenable to testing. Analysis for the other inert gases would lend support to the ^{40}Ar results.

CHAPTER X

SUMMARY AND CONCLUSIONS

This study has revealed a complex history for the pegmatites of the Amelia, Virginia pegmatite district. Emplacement apparently occurred over a period of tens of millions of years into a gradually cooling metamorphic terrain. This long period of high temperatures is expressed in age differences between the Rutherford and Morefield pegmatites, in discordant ages by the K-Ar and Rb-Sr methods, and in a time interval of 10-15 m.y. between crystallization of alkali feldspar in the Rutherford pegmatite and its exsolution to form perthite. A paragenetic sequence was established for the feldspars from the Rutherford pegmatite based on trace element contents. The behavior of the trace elements K, Rb, Sr and excess ^{40}Ar strongly suggest that the crystallization of five albites from this pegmatite took place under closed system conditions. Strontium isotopic evidence indicates assimilation of small quantities of wall-rock which acted to lower the $(\text{Sr}^{87}/\text{Sr}^{86})_0$ ratios of the crystallizing albites. Minor assimilation is substantiated by mineralogical evidence in the pegmatite. As the Rutherford pegmatite crystallized the ^{40}Ar partial pressure gradually increased causing the incorporation of excess

^{40}Ar in quartz, topaz, beryl, and the later albites. Observance of excess ^{40}Ar in minerals with and without fluid inclusions indicates that this site played a minor role in the incorporation of excess ^{40}Ar by Amelia minerals.

Analysis of cogenetic albite-mica pairs from ten pegmatites reveals that six of them contain albites which yield ages older than the reference ages. One of the remaining pegmatites was probably reheated during deposition of Laramide and/or mid-Tertiary volcanics. This re-heating produced significant ^{40}Ar loss from both the albites and muscovite. The quantity of excess ^{40}Ar incorporated by these albites increases with increasing sample age indicating that the excess inert gas age effect exists in albite as well as in the cyclosilicates (Damon and Kulp, 1958).

Heating experiments on natural albites, quartz, topaz, and microcline suggest that the excess ^{40}Ar is not primarily located in fluid inclusions. Albite samples with and without fluid inclusions and microcline showing previous ^{40}Ar loss released approximately the same fraction of the total ^{40}Ar when heated under similar conditions. Apparently a certain fraction of the total ^{40}Ar in albite and microcline is located in a low temperature site regardless of the proportions of excess and radiogenic ^{40}Ar . This observation in feldspars casts considerable doubt on the possibility of removing the excess ^{40}Ar from any sample

by low temperature heating or decrepitation. In microcline as the temperature was increased up to 770°C there was no sudden release of ^{40}Ar as would be expected from the decrepitation of fluid inclusions. Values of D/r^2 increased exponentially over this temperature range according to the equation $D/r^2 = D_0/r^2 \exp (-E/RT)$ where the energy of activation $E = 26$ kcal/mole. Heating experiments on albite, quartz and topaz, also indicate that the ^{40}Ar is located in multiple sites. In topaz for example, a large proportion of the ^{40}Ar was not released until structural breakdown began. Quartz showed significant ^{40}Ar loss after previous heating should have released any ^{40}Ar held in fluid inclusions.

Argon introduction experiments have revealed that large quantities of argon are incorporated by albite at high temperatures even at pressures as low as 1 bar. The introduced argon was shown to be located in at least two sites in the albite. The low temperature site had an energy of activation of about 38 kcal/mole and contained about 14% of the total argon.

This study has presented additional evidence that the micas in pegmatites incorporated little or no excess ^{40}Ar . Potassium-argon ages on micas from the Bob Ingersoll pegmatite and from Elba are concordant with ages obtained by other geochronological methods, although in both cases,

albites incorporated significant quantities of excess ^{40}Ar . The reason for this behavior is unknown. Argon introduction experiments by Gerling et al. (1965) have demonstrated that the micas readily incorporate argon at high pressure. Additional experiments are needed in the low pressure range to clarify this problem.

The quantities of atmospheric ^{40}Ar held by minerals used for potassium-argon dating have been related to the surface area of the mineral. Surface area measurements on lepidolite suggest that atmospheric ^{40}Ar is able to penetrate between the cleavages thus increasing the atmospheric ^{40}Ar content.

It has been suggested that, although the low potassium minerals from pegmatitic environments are not suited for potassium-argon dating because of the widespread presence of excess ^{40}Ar , they may furnish important information on the degree of closure of the system for volatile components. Examination of selected samples with a known paragenesis could indicate whether the system was closed or open or if it had opened at some point during crystallization. This information would contribute significantly to an understanding of pegmatite genesis.

APPENDIX

SAMPLE DESCRIPTIONS

AWL-5-65a- Rutherford Mine, Amelia, Virginia, Reticulated, clear crystals of clevelandite up to 3/4 inch in length. Contains abundant muscovite intergrown with albite. Crushed to -35 +48 mesh.

AWL-5-65m- Rutherford Mine, Amelia, Virginia, Muscovite in 1/8 inch to 1/4 inch flakes from AWL-5-65a.

AWL-12-65- Rutherford Mine, Amelia, Virginia, Green microcline perthite (amazonstone) containing 5-10% albite as veinlets and patches. Crushed to -20 +48 mesh.

AWL-13-65- Rutherford Mine, Amelia, Virginia, Blue crystals of albite. Crushed to -48 +100 mesh.

AWL-17-20-65- Rutherford Mine, Amelia, Virginia, Green muscovite crystals approximately 1 1/4 inch in length.

AWL-19-25- Morefield Mine, Amelia, Virginia, Clear blue crystals of albite up to 3/4 inch in length. Crushed to -35 +48 mesh.

AWL-21-65- Rutherford Mine, Amelia, Virginia, Small blue beryl crystals in massive white quartz. Associated with black tourmaline crystals up to 1/2 inch in diameter.

AWL-22-65w.r.- Rutherford Mine, Amelia, Virginia, Green microcline perthite (amazonstone). Sample contained approximately 9% albite as veinlets and exsolution lamellae. Sample crushed and splits taken for K and Ar analysis prior to sieving and separation.

AWL-22-65a- Rutherford Mine, Amelia, Virginia, Albite separated from AWL-22-65w.r. Sample crushed to +150 mesh and separated with heavy liquids.

AWL-22-65m- Rutherford Mine, Amelia, Virginia, Microcline separated from AWL-22-65w.r. Sample crushed to +150 mesh and separated with heavy liquids.

AWL-23-65- Morefield Mine, Amelia, Virginia, Large (4 inch x 3 inch x 1/2 inch) crystal of bronze zinnwaldite. Crushed to +20 mesh.

AWL-24-65- Rutherford Mine, Amelia, Virginia, Large cleavage of moonstone variety of albite containing abundant fluid inclusions up to 0.01 mm in length. Sample crushed to -48 +65 mesh.

AWL-25-65- Rutherford Mine, Amelia, Virginia, Large cleavage of moonstone variety of albite containing abundant fluid inclusions up to 0.01 mm in length. Sample crushed to -48 +65 mesh.

AWL-26-65- Morefield Mine, Amelia, Virginia, Massive white topaz containing abundant fluid inclusions. Sample crushed to -32 +65 mesh.

AWL-30-65- Rutherford Mine, Amelia, Virginia, Massive white quartz from AWL-21-65. Sample crushed to -11 +45 mesh.

AWL-27-65a- Chemalloy Mine, Bernic Lake, Manitoba, Clear, bladed crystals of albite. Sample crushed to -42 +60 mesh.

AWL-27-65L- Chemalloy Mine, Bernic Lake, Manitoba, Small purple flakes of lepidolite. Sample crushed to -42 +80 mesh.

AWL-27-65q- Chemalloy Mine, Bernic Lake, Manitoba, Massive clear quartz. Sample crushed to -60 +80 mesh.

AWL-28-65a- Bobruvka, Nove Mestona, Western Moravia, C.S.S. R., Albite from vuggy pegmatite. Associated with muscovite. Sample crushed to -48 +65 mesh.

AWL-28-65m- Bobruvka, Nove Mestona, Western Moravia, C.S.S. R., Small perfect stepped crystals of muscovite.

AWL-1-66a- Governador Valadares, Minas Gerais, Brazil, Smithsonian Institution sample number R-16178. Albite from vuggy sample of albite, muscovite and minor pyrite and rutile. Sample crushed to -48 +65 mesh.

AWL-1-66m- Governador Valadares, Minas Gerais, Brazil, Muscovite from AWL-1-66a. Crystals range up to 3 inches in size. Smaller crystals are perfect with a silky luster. Crushed to +20 mesh.

AWL-3-66- Bob Ingersoll Mine, Keystone, South Dakota, Large 1 1/4 inch crystal of muscovite from massive sample of muscovite, microcline, albite and columbite. Sample crushed to +20 mesh.

AWL-4-66- Bob Ingersoll Mine, Keystone, South Dakota, Bladed albite from sample of albite, lepidolite, and quartz. Sample crushed to -48 +65 mesh.

AWL-5-66- Canoa Ranch Pegmatite, Sierrita Mountains, Arizona, Massive clear quartz. Sample crushed to -48 +65 mesh.

AWL-6-66- Bontempelli Quarry, Monte Capanne, S. Piero, Elba, Biotite separated from granodiorite. Cleaned 45 minutes in ultrasonic tank.

AWL-10-66- S. Piero, Monte Capanne, Elba, Pink tourmaline from aplitic dike named Filone Di Grotta D'Oggi. Sample was from a pegmatitic cavity in the dike. Sample crushed to -20 +48 mesh.

AWL-11-66- S. Piero, Monte Capanne, Elba, Albite from pegmatitic part of aplitic dike named Filone Della Speranza. Sample crushed to -65 +100 mesh.

AWL-15-66- Pegmatite on hill north of Mica Mill, Wickenburg pegmatite district, Arizona, 33° 57' 45" N, 112° 33' 45" W, Spodumene from center of pegmatite. Sample fresh and unaltered. Sample crushed to -80 +150 mesh.

AWL-16-66- Location as for AWL-15-66, Muscovite center of pegmatite and associated with spodumene.

AWL-18-66- Location as for AWL-15-66, Coarse grained albite with abundant associated tourmaline. Sample collected near inclusion of Yavapai schist above muscovite-spodumene zone. Sample crushed to -60 +80 mesh.

AWL-19-66C- Location as for AWL-15-66, Coarse grained albite from border zone on floor of pegmatite. Sample crushed to -80 +150 mesh.

AWL-19-66F- Location as for AWL-15-66, Sugary albite as 1 inch vein cutting coarse grained albite AWL-19-66C. Sample crushed to -80 +150 mesh.

AWL-20-66a- Location as for AWL-15-66, Albite from albite-tourmaline border zone at west end of pegmatite. Sample crushed to -80 +150 mesh.

AWL-20-66t- Location as for AYL-15-66, Tourmaline from AYL-20-66a, Sample crushed to -80 +150 mesh.

AWL-23-66- Snow Queen Mine, Pala District, near Pauma, California, Muscovite from muscovite, tourmaline, albite, and quartz pegmatite. Sample cleaved into 1/4 - 1/2 inch sheets.

AWL-24-66- Location as for AYL-23-66, Clevelandite albite from albite, muscovite, lepidolite sample. Sample crushed to -48 +65 mesh.

AWL-25-66- Location as for AYL-23-66, Massive clear quartz. Sample crushed to -48 +65 mesh.

AWL-26-66- Chemalloy Mine, Bernic Lake, Manitoba, Clevelandite albite with associated muscovite. Sample crushed to -80 +150 mesh.

AWL-27-66- Chemalloy Mine, Bernic Lake, Manitoba, Spodumene from giant crystal. Minor associated quartz. Sample crushed to -60 +80 mesh.

AWL-28-66- Bob Ingersoll Mine, Keystone, South Dakota, Beryl.

AWL-6-67- Christmas Lake Pegmatite, Beartooth Mountains, Montana, Large 2 1/2 inch crystals of muscovite. Small inclusions of biotite. Sample cleaved into 1/2 inch sheets.

AWL-8-67- Location as for AYL-6-67, Translucent quartz with minor associated potassium feldspar. Sample crushed to -48 +65 mesh.

AWL-10-67- Location as for AYL-6-67, Albite from albite, potassium feldspar, quartz, biotite pegmatite. Sample crushed to -65 +100 mesh.

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