

A STUDY OF LEACHING EFFECTS UPON THE MEASURED AGE
OF A CAMBRIAN GLAUCONITE

by
W. Kirby Gowen, Jr.

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ABSTRACT

Title: A Study of Leaching Effects upon the Measured Age of a Cambrian Glauconite.

Author: W. Kirby Gowen, Jr.

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A single glauconite of Upper Cambrian age from the Birkmose member of the Franconia formation from Wisconsin has been mechanically purified and split into six fractions. Ages have been determined for four of these fractions by using both the Rb/Sr and K/A methods. The four portions were treated in the following manner: G3280A (2a) was leached in 25% HAc for 17 hours, G3280A (4) was heated at 97°C for 25 hours, G3280A (5) was not treated, and G3280A (6) which was composed of fines and contained a large amount of calcium carbonate, was untreated also.

The Rb/Sr age for G3280A (2a) was in excellent agreement with G3280A (4 and 5) although its normal strontium content was reduced from 12 ppm to 8.6 ppm. The K/A ages for G3280A (2a, 4, and 5) showed excellent agreement so that heating, at least at a temperature of 97°C, has no effect on the argon content. The Rb/Sr ratio for G3280A (6) was less than one-tenth of that measured for the other three fractions, and the ages for both the isotope dilution and isotope ratio analyses were highly erroneous. The K/A age for this portion was in excellent agreement with the Rb/Sr ages but thirty-five million years too high for the rest of the K/A ages.

The calculated ages for three of the fractions show good agreement with the Holmes B Time Scale. The age of the Birkmose member of the Franconia formation is 455 (± 20) million years according to the Rb/Sr method. The age, according to the K/A method, is 425 (± 22) million years, but the potassium values may be slightly high. The average age for both methods is 440 (± 20) million years which is in perfect agreement with the Holmes B Time Scale.

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INTRODUCTION

The usefulness of the mineral glauconite as a means of measuring absolute sedimentary rock ages has been explored by several workers. Wasserburg et al (1955) and Lipson (1956) started the K/A work while Herzog et al (1958) began the initial Rb/Sr investigations with Cormier developing this method further as a Doctor's thesis (1956). These analyses which range from Cambrian to Recent in age show good agreement in most cases with Holmes' B Time Scale (Figure 2). A good summary of the previous work done on the age determination of sedimentary rocks has been presented by Herzog et al (1958).

Past studies on the origin and formation of the mineral glauconite by numerous investigators have all shown that certain limiting conditions prevailed. Warshaw (1957) has summarized these conditions as follows:

"The site of formation is in moderately shallow marine waters which are slightly reducing due to decaying organic matter.

"The formation takes place during times of decreased or negligible sedimentation of detrital material.

"After or during formation glauconite is usually reworked by wave action, which may be that of transgressing or regressing seas.

"Glauconite develops largely by the replacement of pre-existing silicates; however the type of source material and manner of its replacement vary.

If glauconite is formed as an alteration product, any radiogenic Sr⁸⁷ present in the original mineral must be removed before the glauconite is formed. An isotope dilution

analysis of a recent sediment glauconite from the North Atlantic Ocean by Cormier showed no measureable amount of radiogenic Sr^{87} .

Measured normal strontium content for the glauconites analyzed by Cormier varied so greatly (from 4.2-163 ppm), and microscopic determinations of the impurities were made. It was found that most of the glauconites observed contained calcium carbonate as a cement coating on the grains or filling cracks within the grains themselves.

To test this hypothesis, Cormier leached a portion of the Isvos glauconite from Leningrad, Russia, with 1.5 N HCl for three minutes while the rest was left untreated. Mass spectrometric determinations on both fractions showed that the normal strontium content had dropped from 28.9 ppm for the untreated portion to 4.2 ppm for the leached portion or by a factor of 7. Because the ages for the two fractions agreed within experimental error (460 and 471 million years), the leaching in this case did not effect the radiogenic $\text{Sr}^{87}/\text{Rb}^{87}$ ratio. According to geologic and paleontologic evidence, the Isvos is Lower Ordovician; but, according to Cormier, it is analytically older than the Franconia formation.

The present investigation was begun with a threefold purpose which is outlined below.

The first purpose was to obtain further information on the effects of leaching of a glauconite with particular

attention paid to the following:

- a. the measured amounts of rubidium to see if there is any loss from acid leaching. A difference could be due to the presence of rubidium in the carbonate cement or the leaching of rubidium from the glauconite itself.
- b. the measured amounts of normal strontium (to determine how much normal strontium) in the untreated portion was contained in the carbonate cement.
- c. the measured amounts of radiogenic strontium to make sure that it was all present in the glauconite and not partly in the cement.
- d. the measured $^{87}\text{Sr}/^{87}\text{Rb}$, which is the ratio used to determine the final age of the glauconite.

The second purpose was to determine an age for the glauconite and the sedimentary rock from which it was taken. By analyzing the glauconite by both the Rb/Sr and K/A methods of age determinations, an excellent opportunity was afforded to test the amount of agreement which could be expected for a glauconite.

The third purpose was to study the effect heating would have upon the argon content of the glauconite. It was believed that diffusion of argon would occur at elevated temperatures.

It was with these purposes in mind that the following specifications were set up.

1. A large sample of at least 100 grams so that all portions would contain at least 20 grams.
2. A high Rb/Sr ratio so that small variations in the radiogenic Sr^{87} content, which is formed from the decay of Rb^{87} , would be measurable with a small analytical error.
3. A well-crystallized glauconite with a basal lattice spacing $d(001)=10.1 \text{ \AA}$.

By using x-ray powder diffraction photographs, Warshaw (1957) has classified glauconites in the following manner:

- a. "well-crystallized" glauconite d(001)=10.1 A
- b. "typical" glauconite d(001)=10.2-10.3 A
- c. "mixed-layer" glauconite d(001)=10.4-11.0 A
- d. "poorly-crystallized" glauconite d(001) 11.0 A

The well-crystallized glauconite occurs as lobate, globular grains in dolomite, chert, or arenaceous rocks, while the less ordered varieties occur as irregular, porous grains.

CHAPTER I. SAMPLE PREPARATION

A. SELECTION OF A GLAUCONITE

A Cambrian glauconite G3280 was selected for the following reasons:

1. Sample is stratigraphically and paleontologically well dated.
2. It was known to have a Rb/Sr ratio of roughly 20 from a previous isotope dilution analysis by Cormier (1956).
3. It was analyzed by x-ray powder diffraction photography (Moore, 1958) and found to have a basal lattice spacing of 10.1 Å.
4. A similar sample has been independently analyzed in another laboratory (Wasserburg and Hayden, 1955).
5. It was of sufficient size (500 grams) to insure that enough pure glauconite would be obtained after mechanical concentration.
6. It also offered an excellent opportunity to refine Cormier's Cambrian and Ordovician ages which ranged from 380-480 million years.

Sample R3280 from Hudson, Wisconsin, was collected by Professor E. Mencher of M.I.T. during the Geological Society of America's Field Trip No. 2, 1956 and came from the Birkmose Member of the Franconia Formation of Upper Cambrian age. This exposure of the Birkmose is described in the Guidebook (Berg 1956) as the type locality. The Franconia formation is shown in Figure I and consists of five members. Starting with the oldest they are: the Woodhill- a cross-bedded, medium to coarse-grained sandstone; the Birkmose- a glauconitic, fine-grained sandstone; the Tomah- a very fine-grained sandstone plus interbedded shale; the Reno-

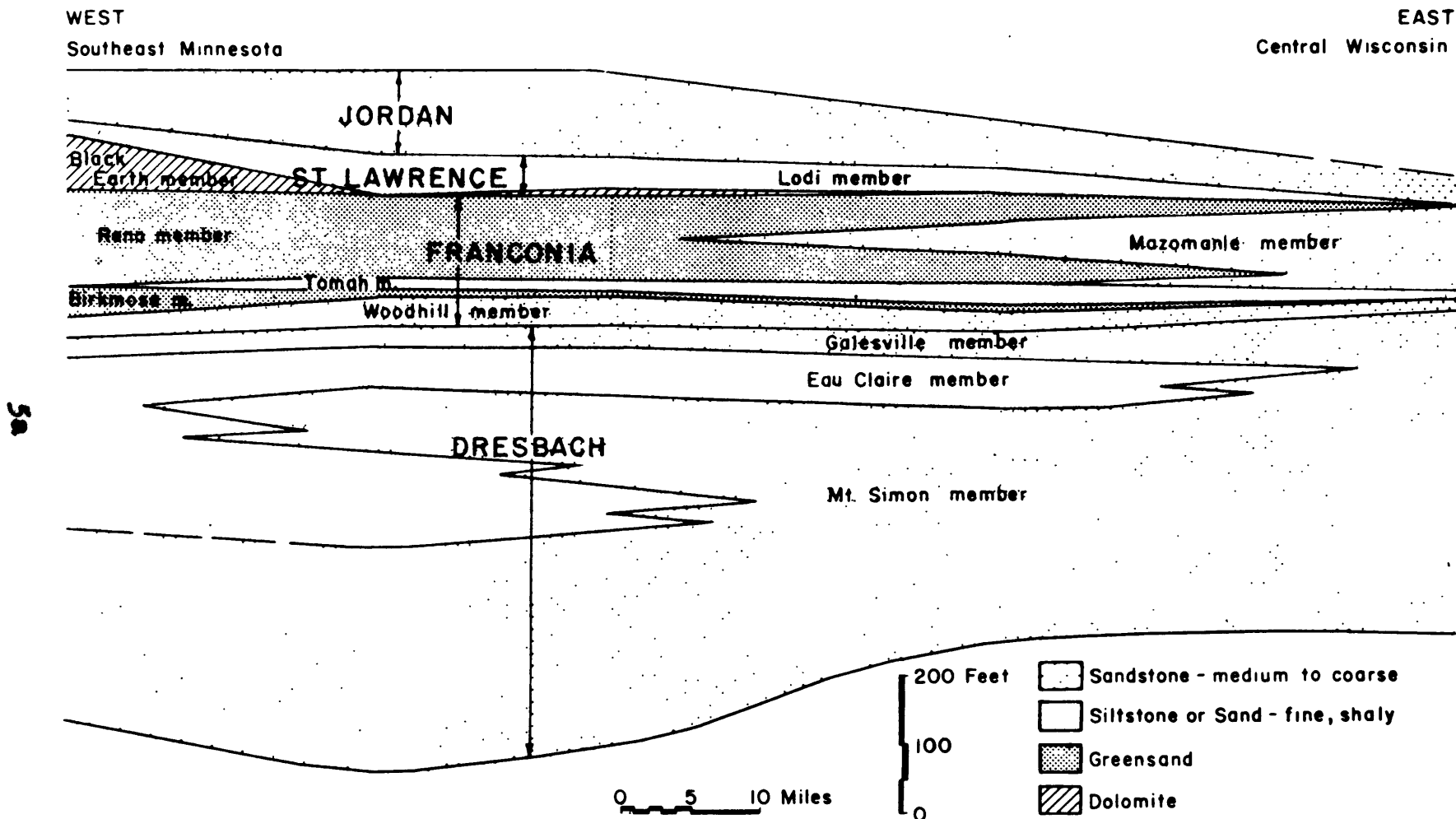


FIGURE I - UPPER CAMBRIAN FORMATIONS

Berg (1956)

a glauconitic, fine-grained sandstone; and the Mazomanie- a thin-bedded or cross-bedded sandstone.

Under the binocular microscope the crushed, untreated sample was seen to consist of 60-70% grass-green glauconite, coated with a reddish-yellow cement. Disseminated quartz grains were also present.

B. MECHANICAL PREPARATION

Student John Moore of M.I.T. did the mechanical separation which is described here. A 500 gram sample was crushed partly by finger, and by rolling under an iron pestle on an iron surface and later on a plastic table top.

The sample was then screened. The +48 mesh size was recrushed, the -48+100 and -100+200 mesh sizes were run through a Frantz magnetic separator, while the -200 mesh size was also retained. Eventually all but about 50 grams passed the +48 mesh screen.

The non-magnetic portion was collected and labeled R3280B. The magnetic portion, composed of approximately 100 grams of glauconite some with a reddish carbonate coating, was collected and labeled G3280A.

The sample was then split into 20 gram portions for the following treatments:

- G3280A (1). This portion was separated in bromoform, whose density was adjusted with acetone, so that quartz floated while dolomite sank. Most of the sample sank.
- G3280A (2). This portion was divided in half.
 - a. Because acetic acid is known to leach carbonate and adsorbed ions on clay, this fraction was leached in 80 ml. of 25% HAc for 17 hours.

- b. This fraction was left in 100 ml.
of demineralized water for 17 hours.

The solutions were stirred once, allowed to sit for 17 hours, and then vacuum filtered. The HAc leached fraction was washed several times, dried in air at a temperature of 35-40°C.

- G3280A (3). This portion was heated for 25 hours at 160°C and lost approximately 0.4 of a gram in weight, probably adsorbed water. This sample was not used because it was felt that a high loss of argon would be encountered.
- G3280A (4). This portion was heated for 25 hours at 97°C and lost approximately 0.3 of a gram in weight.
- G3280A (5). This portion was left untreated.
- G3280A (6). This portion is composed of the -200 mesh fraction of the original sample and was washed in acetone to clean the grains of any minute particles which might be present.

A binocular inspection of the treated samples showed no apparent changes except that the HAc leached fraction contained less carbonate-coated grains.

Of the seven fractions described above, the four listed below were chosen to be analyzed for this study.

- G3280A (2a). This fraction was of prime importance because it would show if leaching the calcareous cement surrounding a mineral affected the radiogenic strontium or rubidium content of the mineral itself. By also measuring the potassium and argon content and comparing it with G3280A (5) any variations in the abundance of either element could be noted.
- G3280A (4). This fraction was chosen to test the effect heating might have upon the argon present in the glauconite. The rubidium, strontium, and potassium concentrations should remain unchanged, these elements not being volatile from silicates at this low temperature.

G3280A (5). This unheated fraction was used as the standard so that any differences in the other portions could be noted.

G3280A (6). This fraction, which was only about 50-60% glauconite, was chosen to study how much a large amount of non-radiogenic strontium, which was present in the carbonate cement, would effect the precision of measurement of the radiogenic strontium content and also the age.

C. CHEMICAL PREPARATION

1.0 gram samples for Sr-Rb isotopic dilution analyses and 0.4 gram samples for K analyses are accurately weighed to ± 0.2 mg. while roughly 3.0 grams are used for the strontium isotopic ratio analyses.

All weighings are then placed in platinum dishes with the isotopic dilution samples receiving a known amount of Sr^{84} and Rb^{87} spike solutions whose compositions and concentrations are given in Tables 1 and 2. The samples are decomposed in reagent grade hydrofluoric and sulfuric acid. The samples are taken almost to dryness, and then 15 ml. more of hydrofluoric are added to make sure that all the silicon has been removed. The samples are then taken to complete dryness.

The isotopic dilution and ratio fractions are taken into solution using a small volume of 6 N. HCl and is heated for over an hour to insure removal of all fluoride ions.

The potassium fractions are taken into solution using a demineralized water solution containing 1.2 ml. of H_2SO_4 per liter. All HCl used in this study has been distilled in vycor glassware and stored in polyethylene bottles. All water has been passed through an ion exchange resin demineralizer and contains less than 0.3 ppm electrolytes as NaCl. Isotopic

dilution analyses of this water disclosed the presence of 0.04 ppm potassium, 0.0005 ppm rubidium, and 0.0003 ppm strontium (Pinson 1958).

Roughly 5 ml. of radioactive Sr^{85} tracer are added to the isotopic dilution and ratio samples before they are placed on the ion exchange columns for monitoring purposes. This tracer was produced by deuteron bombardment of reagent grade rubidium chloride in the M.I.T. cyclotron and has been described by Winchester (1957).

The ion exchange columns were constructed using Dowex 50, 8% cross-linked, 200-400 mesh cation exchange resin. The columns are made of vycor glass one inch in diameter and contain approximately 12" of resin. The columns are eluted with 2 N. HCl throughout. Because rubidium enrichment occurs as the last of the potassium leaves the column, a platinum wire was used to locate the rubidium by monitoring the elution for potassium. The strontium is located by monitoring the column for the Sr^{85} tracer with a Geiger counter. Before being placed on the tantalum filament of the mass spectrometer source, the rubidium is converted to nitrate and the strontium to oxalate. The conversions of rubidium and strontium chloride to nitrate and oxalate respectively have been fully described by Pinson (1957).

Once the potassium fractions have been taken into solution, they are transferred to volumetric pyrex flasks and diluted to exactly 500 ml. with a solution containing 1.2 ml. of sulfuric acid per liter of water. A 50 ml. aliquot of

this solution is pipetted into a volumetric flask and 5 ml. of a standard solution containing 16, 000 ppm lithium is added. The resulting mixture is diluted to 100.0 ml. This solution is then ready for flame photometric analysis. Potassium standards, containing lithium plus synthetic biotite, were prepared using reagent grade potassium phthalate and lithium nitrate and the synthetic biotite described by Pinson (1958). The lithium is used as an internal standard.

CHAPTER II - INSTRUMENTATION AND ISOTOPIC ABUNDANCES

A. MASS SPECTROMETRY

The mass spectrometer used in this study was a Nier type, 60° sector, 6 inch radius, direct-focussing instrument. Thermionic emission is used to produce positive ions which are accelerated between two half plates at a 2500 volt negative potential and passed through a sectored magnetic field of 6" radius and about 4000 gauss. As the ions or charged particles enter the magnetic field they are split into several beams with each representing a certain mass/charge ratio. The beams then continue up the tube; and, as the strength of the magnetic field is varied, the different mass beams pass over the collector slit. The resulting current is amplified by a vibrating reed electrometer (Applied Physics Corporation Model 30) and fed to a Brown strip chart recording potentiometer. A detailed discussion of the mass spectrometer used in this study has been written by Cormier (1956).

B. FLAME PHOTOMETRY AND ARGON SYSTEM

The flame photometer used in this study was a Perkin Elmer Model 146. This instrument was just recently purchased, and for the first set of analyses was not functioning properly. There is still a small amount of drift present in the deflection needle. Because propane gas was recommended for potassium analyses, a tank of propane was adapted

for the photometer. It was used during all of the analyses reported in this study.

The operational procedure is described fully in the Perkin Elmer handbook and will only be briefly outlined here. The flame photometer is turned on 45-60 minutes beforehand. A lithium solution is atomized, and the instrument is adjusted to give the recommended sensitivity. The slope of the curve for the potassium standards is determined, and the instrument is then ready for analysis. The potassium unknowns are run alternately with nearby standards. Although the handbook mentions that no cleaning of the atomizer is necessary between runs (except when it is clogged), a small amount of the next solution to be run was used to clean the atomizer anyway.

Student Stanley Hart of M.I.T. ran the argon analyses reported in this study on the argon system which has been described by Hurley (1957) and (1958).

C. ISOTOPIC ABUNDANCES OF STRONTIUM AND RUBIDIUM AND CALIBRATION OF SPIKES

A number of pure Sr^{84} and Rb^{87} spike samples have been mass spectrometrically analyzed by this laboratory in order to determine the relative abundances of the isotopes in the spikes. These values are listed in Table 1. All samples analyzed in this work were spiked with the same Rb^{87} and Sr^{84} spike solutions, in the concentrations shown in Table 2.

The normal relative abundances of rubidium and strontium

isotopes shown in Table 1 are those reported by Nier (1950) and Bainbridge and Nier (1950). For the age calculation on Sr^{87} relative abundance of 0.0700, instead of 0.0702 was used, on the basis of Herzog and Pinson's (1956) and Schumacher's (1956) calculated value of 0.0683 ± 0.0010 for the abundance of Sr^{87} in total terrestrial strontium 4.7 billion years ago and Bainbridge and Nier's (1950) calculated value of 0.0702 for the relative abundance of Sr^{87} in terrestrial strontium today. A graph was drawn up with the change in Sr^{87}/Sr plotted as a function of time. It was from this graph that the normal Sr^{87} abundance used in this study was taken.

TABLE 1

<u>ISOTOPIC ABUNDANCES OF STRONTIUM AND RUBIDIUM</u>				
	<u>Sr 84</u>	<u>86</u>	<u>87</u>	<u>88</u>
Sr^{84} Spike	0.5348	0.1403	0.0424	0.2826
Normal	0.0056	0.0986	0.0702	0.8256
	<u>Rb 85</u>	<u>87</u>		
Rb^{87} Spike	0.0450	0.9550		
Normal	0.7215	0.2785		

Because the quantities of spike obtained from the Atomic Energy Commission are small and therefore the error in weighing great, it is necessary to calibrate them. The calibration is explained in detail by Cormier (1956) and

will only be outlined here. Large amounts (0.2 grams) of reagent grade normal rubidium are weighed out and put into solution separately. This makes any error in weighing negligible. Aliquots of these solutions are then mixed with a known amount of the Rb^{87} and Sr^{84} spike solutions and analyzed on the mass spectrometer. The calibrated concentrations of the spike solutions used are given in Table 2.

TABLE 2

CALIBRATED SPIKE CONCENTRATIONS

<u>Spike Solution</u>	<u>Concentration</u>
Sr^{84} Spike	19.8 $\mu\text{g/ml}$
Rb^{87} Spike	57.8 $\mu\text{g/ml}$

CHAPTER III - TREATMENT OF RUBIDIUM-STRONTIUM DATA

As only one ion beam strikes the collector slit of the mass spectrometer at any given time, it is possible to record the various peaks in succession on the Brown strip chart recorder. A large number of sets of peaks are necessary in order to correct for the small variations which occur in the ion currents. A single sweep across the mass range of the element is called a set. A rubidium set would be composed of two peaks; a strontium set of four peaks. From 25-60 sets were collected for rubidium analyses while from 50-120 sets were collected for strontium analyses.

The peak heights were measured using a 50-scale engineering ruler and averaged in pairs to compensate for the rising or falling in ion current strength which is usually present. The pair averages are then used to calculate the following ratios: 85/87 for rubidium and 84/88, 86/88, 87/88, and 87/86 for strontium. These ratios are then tallied, a grand average for each for the whole run is calculated, and this is the number used to determine the amounts of rubidium and strontium in the isotope dilution and ratio analyses.

A. CALCULATION OF NORMAL RUBIDIUM AND STRONTIUM

In order to calculate a Rb/Sr age for a mineral it is first necessary to determine the radiogenic $\text{Sr}^{87}/\text{Rb}^{87}$ ratio. The total rubidium and Rb^{87} present are obtained from the rubidium isotope dilution analysis in the following manner:

If: N=number of atoms of normal rubidium present
 S=number of atoms of spike rubidium present
 and the relative abundances of Rb⁸⁵ and Rb⁸⁷
 given in Table 1 are used

Then: total Rb⁸⁵ atoms=0.7215N+0.0450S
 total Rb⁸⁷ atoms=0.2785N+0.9550S

For the analysis of G3280a (4), the measured 85/87
 ratio of the spiked Rb was 0.5267. This analysis is
 referred to as G3280A (4) Rb IDI (a), signifying the first
 isotope dilution analysis of this sample.

Then: $0.5267 = \frac{0.7215N + 0.0450S}{0.2785N + 0.9550S}$

Cross multiplying: $0.1467N + 0.5030S = 0.7215N + 0.0450S$

Collecting terms: $0.5748N = 0.4580S$

and $N/S = 0.7968$ the atomic ratio of normal to spike

A difference in atomic weight of normal rubidium and spike
 rubidium due to the difference in their isotopic compositions
 makes it necessary to multiply the atomic ratio by a weight
 factor obtained by dividing the atomic weight of normal
 rubidium by the atomic weight of spike rubidium. This
 weight factor is 0.9844.

Then, $N_w/S_w = 0.7968 \times 0.9844 = 0.7844$

Since 5 ml. of Rb⁸⁷ spike of concentration 57.8 µgm/ml
 were added to the sample,

$N_w = 0.7844 \times 5 \times 57.8 = 226.7 \text{ µgm Rb}$

Dividing by the weight of the sample, the concentration
 of rubidium is found to be:

$\frac{226.7 \text{ µgm.}}{1.0017 \text{ gm.}} = 226.3 \text{ ppm Rb}$

Rb IDI (b) for G3280A (4), a second rubidium run, gave 226.9 ppm Rb.

Since Rb⁸⁷ is 28.32% of the total rubidium by weight the amount of Rb⁸⁷ present in this sample would be:

$$\frac{226.3 + 226.9}{2} \times 0.2832 = 64.2 \text{ ppm Rb}^{87}$$

The strontium isotope dilution analysis is run primarily to determine the amount of normal strontium present in the sample and is calculated in the same manner as the rubidium.

If: N=number of atoms of normal strontium present
S=number of atoms of spike strontium present
and the relative abundances of Sr⁸⁴ and Sr⁸⁸ listed in Table 1 are used

Then: total Sr⁸⁴ atoms = 0.0056N + 0.5348S and
total Sr⁸⁸ atoms = 0.8256N + 0.2826S

If: the measured 84/88 ratio for G3280A (4)
Sr IDI = 0.9961

$$\text{Then: } 0.9961 = \frac{0.0056N + 0.5348S}{0.8256N + 0.2826S}$$

Cross multiplying and collecting terms,

$$0.8168N = 0.2533S$$

and N/S = 0.3101 the atomic ratio

Since the $\frac{\text{weight of normal Sr}}{\text{weight of spike Sr}} = 1.0253$

$$\text{Then: } N_w/S_w = 0.3101 \times 1.0253 = 0.3179$$

Although the 84/88 ratio is used to calculate the normal strontium present in the sample because the 84 and 88 peaks are usually about the same height and are representative of the spike and normal strontium concentrations, a

good check on the overall run is to calculate the N/S ratio using the 86/88 ratio from the isotope dilution analysis. These ratios yield ages which agree within a few percent, but the age based on the 84/88 measurement is considerably more reliable because the concentrations of the 86 isotope in the spike and normal strontium are about the same.

Using the relative strontium 86 and 88 abundances from Table 1 and the measured 86/88 ratio for G3280A (4) Sr IDI, the N/S ratio was found to be:

$$N/S = 0.3060$$

The difference between this and the 84/88 N/S ratio is:

$$\frac{0.004}{0.308} \times 100 \approx 1.3\%$$

Since 2 ml. of 19.8 $\mu\text{gm/ml}$. Sr^{84} spike was added to the 1.0017 gm sample, the total amount of normal strontium would be:

$$\frac{2 \times 19.8 \times 0.3179}{1.0017} = 12.6 \text{ ppm}$$

B. CALCULATION OF RADIOGENIC STRONTIUM

The radiogenic Sr^{87} can be calculated using the isotope dilution analysis if there is no rubidium present or if the ratio of 85/87 in the contaminating rubidium is known approximately. This ratio is difficult to know because of memory effects which are present in the mass spectrometer from previous runs. There was rubidium contamination throughout the entire isotope dilution run for G3280A (4) Sr IDI; but comparisons, between the end of the run where

the rubidium was almost gone and the beginning of the run, made it possible to approximate the 85/87 ratio for rubidium to be about 2. The maximum error in age this assumption could lead to is roughly 10%; but, since a separate isotope ratio analysis of the unspiked Sr is made, this error is not introduced. The isotopic dilution analyses for G3280A (6) and G3280A (2a) both contained sets, free of contaminating rubidium, which were used to calculate the isotopic dilution age of each. Rubidium contamination in G3280A (5) persisted throughout the run and made the calculation of an isotope dilution age for this sample impossible to do with any degree of accuracy. Using this correction factor of 1/2 for the measured 87 peaks of G3280A (4), an 87/88 ratio was found to be 0.1364. Because part of the Sr⁸⁷ atoms present in this run are contributed by the radioactive decay of Rb⁸⁷, it is necessary to introduce a third term (R) equal to the number of atoms of radiogenic strontium present.

Using the relative strontium 87 and 88 abundances from Table 1, the

$$\begin{aligned} \text{total Sr}^{87} \text{ atoms} &= 0.0700N + 0.0424S + R \text{ and} \\ \text{total Sr}^{88} \text{ atoms} &= 0.8256N + 0.2826S \end{aligned}$$

$$\text{Then: } 87/88 = 0.1364 = \frac{0.0700N + 0.0424S + R}{0.8256N + 0.2826S}$$

Cross multiplying and collecting terms

$$0.0426N = 0.0039S + R$$

$$R = 0.0426N - 0.0039S$$

But $N = 0.3101S$ from the 84/88 N/S calculation

$$\text{Substituting: } R = (0.0426 \times 0.3101) S - 0.0039S$$

$$R = (0.0132 - 0.0039) S = 0.0093S$$

$$R/S = 0.0093$$

The $\frac{\text{atomic weight of radiogenic Sr}}{\text{atomic weight of spike Sr}} = 1.017$

and the atomic R_w/S_w = 0.0093 x 1.017 = 0.00946

The total amount of radiogenic strontium would be:

$$\frac{0.00946 \times 39.6 \text{ } \mu\text{gm}}{1.0017 \text{ gm}} = .374 \text{ ppm}$$

The more accurate method for determining the radiogenic strontium content of a mineral is to supplement the isotopic dilution analysis with an isotopic ratio analysis and calculate an 87/86 ratio for the unspiked sample. The amount of common strontium is still determined by isotopic dilution analysis.

The 87/86 ratio for G3280A (4) Sr IDI was 1.0381.

Then using the equation:

$$R = 0.0969 \times \text{Sr} \times (87/86 - 0.7099) 1.0116$$

Where R = the radiogenic Sr⁸⁷ = (*Sr⁸⁷)

0.0969 = weight abundance of Sr⁸⁶ in common strontium

Sr = amount of normal strontium present = 12.6 ppm

87/86 = found by mass spectrometric analysis = 1.0381

0.7099 = initial atomic 87/86 ratio present in the mineral

1.0116 = the ratio of the atomic weight of Sr⁸⁷ to the atomic weight of Sr⁸⁶

The radiogenic strontium concentration would be:

$$0.0969 \times 12.6 \times (1.0381 - 0.7099) 1.0116 = 0.405 \text{ ppm}$$

The radiogenic Sr⁸⁷ concentration of an isotopic ratio analysis is more accurate for the following reasons:

a. In an isotope dilution analysis the measured amount of Sr⁸⁷ is dependent not only on the amount of normal and radiogenic Sr⁸⁷ present in the glauconite but also on the

amount of Sr^{87} in the spike which is added. If the isotopic abundance of Sr^{87} in the spike is not known with great accuracy, it would have a noticeable effect upon the radiogenic strontium concentration determined.

b. Since the radiogenic strontium is assumed to be present only in the glauconite, not in the contaminating carbonate, any addition (2 ml. of Sr^{84} spike) to the total amount of strontium measured causes the ratio of radiogenic strontium to total strontium to decrease and introduces greater error. The isotopic ratio analysis has no Sr^{84} spike added.

c. If the calcareous cement surrounding a grain is leached away and the radiogenic strontium content of the grain itself is not disturbed, then the total amount of common strontium measured will be reduced. The percentage of radiogenic strontium to total strontium present would be increased, and the precision of measurement would also be improved.

C. CALCULATION OF AN AGE

Now that the $^*\text{Sr}^{87}/\text{Rb}^{87}$ ratio has been calculated; and, using the decay constant determined by Aldrich (1956), the age for G3280A (4) can be calculated.

$$\text{If: } t = \frac{1}{\lambda} \ln \left(1 + \frac{^*\text{Sr}^{87}}{\text{Rb}^{87}} \right)$$

Where t = age of the mineral

$$\lambda = \text{the decay constant} = 1.39 \times 10^{-11} / \text{year}$$

$$^*\text{Sr}^{87} = \text{radiogenic } \text{Sr}^{87} = 0.405 \text{ ppm}$$

$$\text{Rb}^{87} = 64.2 \text{ ppm}$$

$$\text{Then: } t = \frac{1}{1.39 \times 10^{-11}} \ln \left(1 + \frac{0.405}{64.2} \right)$$

$$\begin{aligned}
&= 0.7194 \times 10^{11} \ln(1.00631) \\
&= 0.7194 \times 10^{11} \times 0.00630 \\
&= 453 \times 10^6 \text{ years}
\end{aligned}$$

D. CALCULATION OF STANDARD ERRORS

The errors used for the various ratios, isotopic compositions, and spiking have been arrived at by running duplicate samples, standardizing laboratory procedures, interlaboratory checks on analyses, running occasional contamination checks, and by calculating the standard deviations for a large number of samples which have been run in this laboratory.

They are:

error in measurement ratios $\approx 0.5\%$
 error in isotopic composition of spike and normal element
 $\approx 0.25\%$

error in spike $\approx 2\%$

$$84/88 = 0.9961 (\pm 0.005) = \frac{0.0056N(\pm 0.0025) + 0.5348S(\pm 0.0025)}{0.8256N(\pm 0.0025) + 0.2826S(\pm 0.0025)}$$

$$\text{Cross multiplying: } 0.8224 + 0.2815S = 0.0056N + 0.5348S$$

$$\begin{aligned}
\text{Error in } 0.8224 &= 0.8224 \sqrt{(0.005)^2 + (0.0025)^2} \\
&= 0.0046
\end{aligned}$$

$$\begin{aligned}
\text{Error in } 0.2815 &= 0.2815 \sqrt{(0.005)^2 + (0.0025)^2} \\
&= 0.0016
\end{aligned}$$

$$\text{Error in } 0.0056 = 0.0056(0.0025) = 0.00001$$

$$\text{Error in } 0.5348 = 0.5348(0.0025) = 0.0013$$

Collecting terms and adding errors,

$$0.8168N(\pm 0.0046) = 0.2533S(\pm 0.0029)$$

$$N/S = 0.3101$$

$$\text{Error in N/S} = 0.3101 \sqrt{\left(\frac{0.0046}{0.8168}\right)^2 + \left(\frac{0.0029}{0.2533}\right)^2}$$

$$= .0040$$

$$\text{and N/S} = 0.3101(\pm 0.0040)$$

Converting to weight ratio

$$\text{Nw/Sw} = 0.3101(\pm 0.0040) \times 1.0253 = 0.3179(\pm 0.0041)$$

The error in the spike = 39.6 (± 0.79) μg

$$\text{Nw} = 0.3179 \times 39.6 = 12.6$$

$$\text{Error in Nw} = 12.6 \sqrt{\left(\frac{0.79}{39.6}\right)^2 + \left(\frac{0.0041}{0.3179}\right)^2}$$

$$= \pm 0.30$$

Since the error in sample weight is negligible compared to those already mentioned, the concentration of normal strontium is:

$$\frac{12.6}{1.0017} \frac{(\pm 0.30)}{1.0017} = 12.6(\pm 0.3) \text{ ppm}$$

The error in the rubidium concentration was calculated in the same way as the normal strontium and is given below.

$$\text{Total Rb} = 226.6(\pm 4.9) \text{ ppm and}$$

$$\text{Rb}^{87} \text{ concentration} = 0.2832 \times 226.6(\pm 4.9) = 64.2(\pm 1.4) \text{ ppm}$$

Assuming a maximum error of ($\pm 1\%$) in the measured 87/88 ratio for G3280A (4) Sr IDI, the error in radiogenic strontium content for this analysis was found to be 0.374(± 0.038) ppm or 10.4%.

Using an error of ($\pm 0.5\%$) for the measured and normal 87/86 ratios, the error in radiogenic strontium content for the isotopic ratio analysis was found to be 0.405(± 0.0144) ppm or 3.6%. The error in the age of this sample is calculated

in the following manner.

$$\begin{aligned} \text{If: } t &= \frac{1}{1.39 \times 10^{-11}} \ln \left(1 + \frac{0.405(\pm 0.0144)}{64.2(\pm 1.4)} \right) \\ &= 453 \times 10^6 \text{ years} \end{aligned}$$

The error in age would be:

$$\begin{aligned} &453 \times 10^6 \sqrt{\left(\frac{0.0144}{0.405}\right)^2 + \left(\frac{1.4}{64.2}\right)^2} \\ &= \pm 19 \times 10^6 \text{ years} \quad \text{or } 4.2\% \end{aligned}$$

But according to Gast (1957) as the number of analyses increases the error decreases by $\frac{1}{\sqrt{K}}$ where K equals the number of analyses.

Although the three samples G3280A (2a), (4), and (5) were not intended to be repetitions at the start of this study, it is now apparent that their total rubidium to total strontium ratios are all quite similar, approximately twenty to one. For this reason they can be considered as a triplicate analysis of G3280A, and the formula Gast refers to can be applied.

$$\frac{1}{\sqrt{K}} = \frac{1}{\sqrt{3}} = 0.5774$$

The error for the three runs would then be

$$0.5774 \times 4.2\% = 2.4\%$$

The error in age would be $\pm 11 \times 10^6$ years.

CHAPTER IV. - TREATMENT OF POTASSIUM-ARGON DATA

In order to calculate a potassium-argon age, it is necessary to determine the ratio of A^{40}/K^{40} in the sample.

Sample G3280A (4) is used as an example.

$$A^{40}/K^{40} = \frac{Y \times N \times 10^{-10}(1-0.1058*R) (39.100)}{*R \cdot W \cdot \%K \cdot N \cdot 10^{-2} \times 0.0119 \times 10^{-2}}$$

where Y = number of A^{38} atoms in spike = 87

$$N = 6.02 \times 10^{23}$$

0.1058 = ratio of 40/38 in the spike gas

0.0119×10^{-2} = isotopic abundance of K^{40}

$$*R = 38/40 \text{ ratio after air correction} = 0.311$$

39.100 = atomic weight of potassium

W = weight of sample = 5.00

K = potassium value in per cent = 6.74

Collecting all the constants together into one term

$$= 0.003285$$

$$A^{40}/K^{40} = \frac{0.003285(87)(1-0.1058 \times 0.311)}{0.311 \times 5.00 \times 6.74}$$

$$= 0.0264$$

A. CALCULATION OF AN AGE

The equation used to calculate the age is:

$$t = \frac{1}{\lambda} \ln \left[1 + A^{40}/K^{40} \left(\frac{1+R}{R} \right) \right]$$

where t = age in years

$$\lambda = \text{total decay constant} = 5.28 \times 10^{-10} / \text{year}$$

A^{40}/K^{40} = ratio as determined above = 0.0264

$$R = \text{branching ratio} = 0.118 = \frac{\lambda_e}{\lambda_B}$$

$$\lambda_e = 0.557 \times 10^{-10} / \text{year}$$

$$\lambda_B = 4.72 \times 10^{-10} / \text{year}$$

Substituting,

$$\begin{aligned}t &= \frac{1}{5.28 \times 10^{-10}} \ln \left[1 + 0.0264 \left(\frac{1 + 0.118}{0.118} \right) \right] \\ &= \frac{1}{5.28 \times 10^{-10}} \ln 1.25 \\ &= 424 \times 10^6 \text{ years}\end{aligned}$$

B. CALCULATION OF STANDARD ERROR

The standard error assumed for the measured ratios are:

$$38/40 = \pm 0.1 - 0.3\%$$

$$36/38 = \pm 10\%$$

The overall error in any one argon measurement is believed to be $\pm 2\%$. For runs with an air correction greater than 10% , the error may be as high as $\pm 5\%$. These errors are mostly qualitative and are based on duplicate analyses, agreement with standards, and contamination checks. At present the largest single error in any age is still due to the potassium values. For this reason the project recently purchased a Perkin Elmer Flame Photometer Model 146. Although only a few samples and standards have been analyzed, it has greatly increased the accuracy of potassium determinations and has shown a high degree of reproducibility so far.

By atomizing several different potassium standards over a period of about 30 minutes, a working curve for the standards was set up; and the maximum deviation was found to be 3% . This error is reduced by repetition of analyses. Several analyses of B3207, B3208, and B3209, three biotite standards whose potassium contents have been gravimetrically determined by Goldich (1957), show very good agreement with Goldich's

values.

If the error in chemistry of potassium = $\pm 2\%$ and

the error in determination of potassium = $\pm 3\%$

The overall potassium error = $\pm 3.6\%$ and

If the overall argon error = $\pm 2.0\%$ for G3280A (4)

Then total error = $\pm 4.9\%$ or 21×10^6 years.

CHAPTER V - RESULTS

The results for the four different portions of G3280A analyzed are given in Tables 3, 4, 5, 6, 7, and 8. Tables 3 and 4 give the measured strontium and rubidium ratios, number of sets collected, and sample weight. Tables 5 and 6 contain the potassium and argon measurements. Tables 7 and 8 give the final results for both methods.

In Tables 7 and 8 the radiogenic Sr^{87} and age determinations marked I.D. were calculated from the isotope dilution analyses, while the determinations marked I.R. were calculated from the isotope ratio analyses.

The standard error for rubidium concentrations was found to be roughly 2%, while for normal strontium it was approximately 2.5%. The standard error for any one of the analyses G3280A (2a, 4, or 5) is about 4.2%. The errors reported in Table VII for G3280A (2a, 4, and 5) were based on the formula discussed by Gast (1957) which gives an error of 2.4%.

The standard error for the potassium-argon ages has already been described for G3280A (4). Because of the somewhat higher air corrections necessary for G3280A (2a and 6), maximum argon errors of 4% and 5% respectively were used.

Table 3

RESULTS OF ISOTOPIC DILUTION ANALYSES OF THE GLAUCONITE

Sample No.	Treatment	Weight	Measured Ratios				
			Sr		Rb		
			84/88	86/88	87/88	85/87	
G3280A (2a)	leached (HAc)	1.0069 gms	1.1683 (±0.0052) (60 sets)	0.3492 (±0.0017) (60 sets)	0.1476 (±0.0007) (10 sets)	a) 0.5286 (±0.0026) (47 sets)	b) 0.5305 (±0.0027) (37 sets)
G3280A (4)	heated (97°C)	1.0017 gms	0.9961 (±0.0050) (122 sets)	0.3186 (±0.0016) (122 sets)	0.1364 (±0.0014) (80 sets) (Rb Corrected)	a) 0.5267 (±0.0026) (63 sets)	b) 0.5278 (±0.0026) (31 sets)
G3280A (5)	untreated	1.0050 gms	1.0077 (±0.0050) (60 sets)	0.3170 (±0.0016) (60 sets)	Rb contamination	a) 0.5234 (±0.0026) (39 sets)	b) 0.5176 (±0.0026) (42 sets)
						c) 0.5294 (±0.0026) (27 sets)	
G3280A (6)	matrix	1.0036 gms	0.2990 (±0.0030) (62 sets)	0.1746 (±0.0017) (62 sets)	0.0961 (±0.0010) (62 sets)	a) 0.3379 (±0.0017) (42 sets)	

All samples were spiked with: 2.0 ml of Sr⁸⁴ spike, containing 19.8 μgm spike/ml
5.0 ml of Rb⁸⁷ spike, containing 57.8 μgm spike/ml

Table 4

RESULTS OF ISOTOPIC RATIO ANALYSES OF UNSPIKED STRONTIUM FROM THE GLAUCONITE

Sample No.	Weight	Measured Ratios		
		87/86	86/88	84/88
G3280A (2a)	3 gms	1.1964 (54 sets) (± 0.0060)	0.1192 (19 sets) (± 0.0012)	0.0075 (18 sets) (± 0.0001)
G3280A (4)	3 gms	1.0381 (105 sets) (± 0.0052)	0.1206 (26 sets) (± 0.0012)	0.0075 (26 sets) (± 0.0001)
G3280A (5)	3 gms	1.0458 (103 sets) (± 0.0052)	0.1190 (26 sets) (± 0.0012)	0.0072 (26 sets) (± 0.0001)
G3280A (6)	2 gms	0.7325 (74 sets) (± 0.0037)	No 88 peaks were scanned	No 84 or 88 peaks were scanned

Table 5

RESULTS OF POTASSIUM ANALYSES OF THE GLAUCONITE

Sample No.	Weight (g/l)	*K concentration (in ppm)	%K		Average %K
G3280A (2a)	0.4030	27.0	6.70	6.81	6.75
		27.97	6.94		
		27.4	6.82		
		27.5	6.80		
	0.4198	28.1	6.69		
G3280A (4)	0.3919	26.4	6.74	6.74	6.74
		**26.37	6.74		
	0.4047	27.3	6.75		
G3280A (5)	0.3793	25.8	6.80		6.77
	0.4048	27.3	6.74		
G3280A (6)	0.4067	15.2	3.74		3.76
	0.4100	15.55	3.79		

* The K concentration is taken from the working curve which plots the concentration as a function of the internal standard reading.

** This analysis was run by Stanley Hart of M.I.T.

Table 6

RESULTS OF ARGON ANALYSES OF THE GLAUCONITE*

Sample No.	Weight	R (uncorrected)	Y	Air Correction	Net R	^{A40} (in std. cc.)
G3280A (2a)	4.00 gms	0.348	86	9.2%	0.377	1.225×10^{-4}
G3280A (4)	5.00 gms	0.296	87	4.5%	0.311	1.210×10^{-4}
G3280A (5)	5.00 gms	0.299	86	1.3%	0.304	1.226×10^{-4}
G3280A (6)	4.00 gms	0.522	85	13%	0.60	0.744×10^{-4}

* All argon analyses reported here were run by Stanley Hart of M.I.T.

Table 7

FINAL RESULTS FOR BOTH METHODS

Sample No.	(ppm by wt)			*Sr (ppm by wt)		*Sr ⁸⁷ /Rb ⁸⁷		% K	A ⁴⁰ /K ⁴⁰
	Rb	Rb ⁸⁷	Sr	I.D.	I.R.	I.D.	I.R.		
G3280A (2a)	226.8	64.2	8.6	0.416	0.410	0.00647	0.00637	6.75	0.0266
G3280A (4)	226.6	64.2	12.6	0.374	0.405	0.00582	0.00630	6.74	0.0264
G3280A (5)	223.7	63.4	12.2	-----	0.402	-----	0.00633	6.77	0.0266
G3280A (6)	125.5	35.5	**80.9	**0.1365	**0.179	**0.00384	**0.00503	3.76	0.0289

** Used Sr⁸⁶/Sr⁸⁸ ratio to compute N/S ratio because of contamination in the 84 peaks.

Table 8

SUMMARY OF AGES BY BOTH METHODS FOR THE GLAUCONITE

Sample No.	Rb/Sr		K/A
	I.D.	I.R.	
G3280A (2a)	465(\pm 30) x 10 ⁶ yrs	458(\pm 11) x 10 ⁶ yrs	426(\pm 26) x 10 ⁶ yrs
G3280A (4)	419(\pm 44) x 10 ⁶ yrs	453(\pm 11) x 10 ⁶ yrs	424(\pm 21) x 10 ⁶ yrs
G3280A (5)	----	455(\pm 11) x 10 ⁶ yrs	426(\pm 21) x 10 ⁶ yrs
G3280A (6)	*276(\pm 180) x 10 ⁶ yrs	*362(\pm 120) x 10 ⁶ yrs	460(\pm 31) x 10 ⁶ yrs

* Used Sr⁸⁶/Sr⁸⁸ ratio for N/S ratio computation.

A. DISCUSSION OF RESULTS

The glauconite ages for the Franconia reported in Table 8 compare very favorably with those listed in Table 9. There are two glauconitic members present in the Franconia formation so that an exact comparison between the ages listed in the two tables is not possible.

TABLE 9

OTHER GLAUCONITE AGES FOR FRANCONIA FORMATION

<u>Analyst</u>	<u>Geologic Age</u>	<u>*Sr⁸⁷/Rb⁸⁷Age</u>	<u>K⁴⁰/A⁴⁰Age</u>
Cormier (1956)	Middle Upper Cambrian	436 x 10 ⁶ yrs.	
Wasserburg & Hayden (1955)	Middle Upper Cambrian		+460 x 10 ⁶ yrs.

+A branching ratio of 0.118 was used

G3280A (2a). The strontium and rubidium analyses for this sample were quite good. The close agreement between the measured *Sr⁸⁷ content for the isotopic dilution and ratio analyses supports this fact. The calculated 86/88 ratio (0.1192) for the isotope ratio analysis shows good agreement with the accepted value of 0.1194 (Bainbridge and Nier, 1950). The 87/88 ratio for the isotopic dilution analysis was calculated using the rubidium free portion of the run.

One of the potassium solutions was run four times because during the second set of analyses the galvanometer needle started drifting badly.

The portion analyzed for argon was placed in the furnace

and outgassed at room temperature overnight. None of the samples placed in the furnace were outgassed at elevated temperatures prior to fusion.

G3280A (4). The duplicate rubidium analyses show excellent agreement. The strontium isotope dilution run contained rubidium contamination throughout. In order to calculate an age for this run, a rubidium 85/87 ratio had to be estimated, and the measured 87 peaks had to be corrected for by subtracting the amount of Rb^{87} present. The emission, during the strontium isotope ratio analysis, was somewhat erratic as witnessed by the strontium 86/88 ratio of 0.1206 as compared to the normal value of 0.1194.

The potassium analyses for this sample showed excellent agreement. The portion analyzed for argon was put in the furnace and pumped on for four and one-half days with no heating.

G3280A (5). The rubidium analyses for this portion show greater variation than the two portions above but are still in good agreement. The strontium isotope dilution analysis contained rubidium contamination throughout; and, because no rubidium peaks were scanned before the strontium emission started, the calculation of an age using this analysis would have a very large error. The strontium isotope ratio analysis for this portion was steady, and the strontium shows excellent agreement.

The potassium analyses show good agreement. The argon portion was allowed to outgas overnight at room temperature under vacuum.

G3280A (6). The rubidium concentration is based on only one analysis. Two earlier attempts to analyze the rubidium content failed when the filament on the mass spectrometer burned out before the samples could be run. The strontium isotope dilution analysis was a very good run with excellent resolution and no rubidium contamination from start to finish. The strontium isotope dilution analysis was a very good run with excellent resolution and no rubidium contamination from start to finish. The strontium isotope ratio run was fair. Because no strontium 88 peaks were collected, no 86/88 ratio could be calculated to check against the normal strontium 86/88 ratio.

The potassium analyses show good agreement. The argon portion was placed in the furnace and allowed to pump overnight.

B. CONCLUSIONS

1. The Rb/Sr ages for G3280A (2a, 4, and 5) show excellent agreement and prove that the acetic acid leaching for seventeen hours had no effect on the age of this particular glauconite. The rubidium and radiogenic strontium content remained unchanged while the normal strontium content was lowered from 12 ppm to 8.6 ppm. By reducing the common strontium present, the percentage of $^{87}\text{Sr}/\text{Sr}$ is increased and the precision of measurement should be improved. Because of the large amount of calcium carbonate present, the matrix portion gave a much lower Rb/Sr ratio (<2) than the other three analyses which gave ratios of about 20. This low ratio caused the errors to range from 32% for the isotope ratio age to over 100% for the isotope dilution age and made them

completely unreliable.

a. The K/A ages for G3280A (2a, 4, and 5) also show excellent agreement and prove that heating at 97°C for twenty-five hours does not effect the age. Although the A^{40} content listed in Table 6 for G3280A (4) is roughly 1.3% lower than G3280A (2a and 5), analyst Hart does not attribute this difference to the heating treatment which the sample received. It should also be noted that this fraction was outgassed for four and one-half days prior to being analyzed for argon. The matrix portion gave an age which is in excellent agreement with the Rb/Sr ages but is 35 million years older than the three other K/A analyses. The measured amounts of A^{40} and potassium were both proportionately lower because of the large amount of extraneous calcium carbonate present. This does not appear to have effected the age except to increase the error in the accuracy with which the smaller quantities of argon and potassium can be measured.

3. A plot of the three reliable Rb/Sr and K/A ages on the Holmes B Time Scale (Figure 2), which was taken from Cormier's thesis (1956), shows good agreement. The K/A ages appear to be slightly lower while the Rb/Sr ages are slightly higher. An average of the ages for the two methods gives $440(\pm 20)$ million years which falls right on the line used by Holmes in his time scale.

4. An age for the Birkmose member of the Franconia formation of the Upper Cambrian has been calculated as $455(\pm 20)$ million

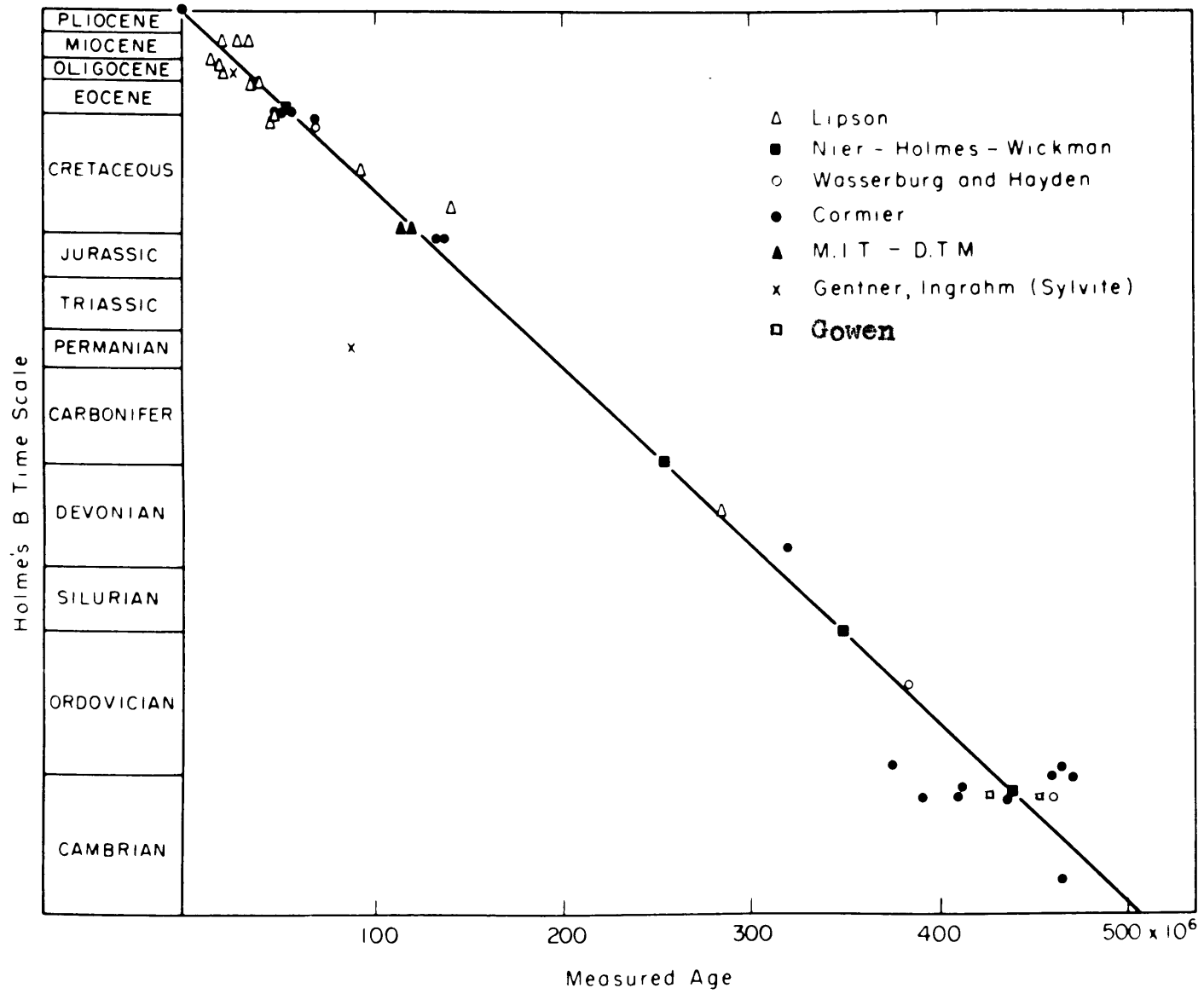


FIGURE 2

years using the Rb/Sr method. An age of 425(\pm 22) million years has been calculated using the K/A method. At present the age calculated by the Rb/Sr method is slightly more accurate because of the uncertainty which is still present in the method used for potassium determination. If the potassium analyses reported in this study are actually 3% high, the calculated ages would all be roughly 12-15 million years older; but the disagreement with Wasserburg and Hayden's K/A age (Table 9) needs further investigation.

C. SUGGESTIONS FOR FURTHER INVESTIGATION

1. Another sample or two from the Birkmose member should be analyzed in order to determine sample to sample reproducibility by both methods of age determination.
2. The portion G3280A (3) should be analyzed now to determine the effect of heating at a higher temperature prior to the argon analysis.
3. A sample from the Reno member, which lies above the Birkmose (Figure 1) should be analyzed to test the precision and degree of resolution which can be obtained by the Rb/Sr and K/A methods.
4. In order to determine just how much material can be leached from a glauconite, several glauconites should be split into three or four portions with all but one being treated by a different strength of hydrochloric or acetic acid. The results from an analysis of this type would be helpful for two reasons:

a) It may show that acids above a certain concentration affect the $^{87}\text{Sr}/^{87}\text{Rb}$ ratio. If this is so, then only acids below that concentration should be used.

b) It may show that acids above a certain strength all leach the same amount of common strontium from the glauconite. If this is so, then one of the weakest of these acids which leach the same amount could be used as a standard to leach all glauconites.

5. Professor Pinson of MIT has suggested setting up a column similar to an ion exchange column using a glauconite in place of the resin. This glauconite would then be continuously eluted with an acid for several hours. This experiment sounds like an excellent idea because it would simulate the action of ground water as it flows through a permeable bed.

6. Glauconites of different lattice spacings (some of the less ordered varieties) should also be leached and analyzed by both methods. The poorly crystallized varieties are likely to show a much greater spread between methods because of the probability that loss of the elements from the glauconite itself is more likely to occur.

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