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RUBIDIUM-STRONTIUM AGES OF GLAUCONITE AND THEIR APPLICATION TO THE CONSTRUCTION OF AN ABSOLUTE POST-PRECAMBRIAN TIME SCALE

by

RANDALL F. CORMIER

S.B., Saint Francis Xavier University

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Certified by...
Thesis Supervisor

....
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ABSTRACT

Title: Rubidium-Strontium Ages of Glauconite and their
Application to the Construction of an Absolute
Post-Precambrian Time Scale.

Author: Randall F. Cormier.

Submitted to the Department of Geology and Geophysics on October 9 , 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

An attempt has been made to measure the absolute ages of sedimentary rocks through the analysis of common strontium, radiogenic strontium, and rubidium contained in glauconite samples separated from sediments. The analyses were carried out using the stable isotope dilution method. In all cases, the sedimentary rocks employed were well dated, geologically, on the basis of index fossils. The periods represented by the glauconites analysed were Cambrian, Ordovician, Devonian, Jurassic, Cretaceous, Eocene, and Recent.

The rubidium content of glauconite was found to range from 180 to 320 ppm. This is rather low in comparison to other minerals being used for Rb/Sr age determinations. The relatively low rubidium contents give rise to low radiogenic strontium contents ranging from zero for the recent sample to a high of 0.54 ppm. Although, in many cases, the common strontium content was found to be between 30 and 100 ppm., it was felt that the major portion of common strontium encountered was the result of carbonate impurities in the sample. A glauconite leached for three minutes in very dilute HCl was found to contain only 4.2 ppm. common strontium while the same sample, unleached, was found to contain 28.9 ppm.

Because of the low radiogenic strontium contents encountered, isotope abundance determinations were made on unspiked strontium samples extracted from each glauconite. It was found that by doing this, significantly more accurate radiogenic strontium contents, as compared to those utilizing only strontium isotope dilution data, were obtained.

It was found that glauconite in solution could not be analysed directly for rubidium content with confidence, because of contamination rubidium introduced within the mass spectrometer itself. To overcome this difficulty, separation of the rubidium, before analysis, utilizing ion exchange techniques, was employed.

The ages obtained for five Cambrian samples ranged from 392 million years for Upper Cambrian to 584 million years for what probably was an upper Precambrian ~~ies~~ sample. A lowest Ordovician sample from Sweden gave an age of 355 million years

while two Lower Ordovician samples from the Leningrad area of Russia gave ages of 465 to 464 million years. The single Devonian sample analysed gave an age of 321 million years for the Lower Devonian. Two Upper Jurassic samples from the Laramie Basin of Wyoming gave ages of 135 and 138 million years. Three Upper Cretaceous - Lower Eocene samples resulted in ages of 71, 59 and 55 million years. A recent glauconite from the Atlantic Ocean off Georges Bank gave an age of zero.

The glauconite Rb/Sr ages obtained have been compared with U/Pb, K/A, and Rb/Sr age determinations made by other investigators on materials whose geologic ages were thought to be well known, on the basis of either paleontology or igneous-sedimentary relationships. The measured ages, including those by other investigators, have also been compared to the B-time scale set up by Arthur Holmes in 1947. The comparison showed that out of 37 measured ages, 29 were in excellent agreement with Holmes' scale. Of the eight which were not, six were Rb/Sr glauconite ages, one was a K/A glauconite age, and one was a K/A sylvite age (Inghram). On the basis of replicate analyses, it appeared that the apparently discrepant glauconite ages were not the result of analytical error, and it was concluded that processes operative after or during the formation of glauconite were probably responsible. Possible natural processes which would result in discrepant glauconite Rb/Sr ages were examined and discussed.

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INTRODUCTION

The setting up of an absolute time scale for the different events which have taken place on the face of the earth since it was formed has been the objective of a large number of geologists, geophysicists, and others interested in the earth sciences. The first steps taken toward this goal were made by paleontologists and stratigraphers. The fact that organisms had undergone a process of evolution was early recognized, and enabled men to construct a relative time scale for the events in the earth's history in those areas of the world where recognizable fossils could be found in the sedimentary column. Paleontology alone, however, valuable as it has proved to be, suffers from a number of important drawbacks. In the first place, the dating and correlation of strata on the basis of fossil content alone can only be used for the construction of a relative time scale, no absolute ages being determinable. Secondly, a relative time scale based on paleontology can be set up for only about 15% of the entire history of the earth, that is, from the base of the Cambrian to the present. This is, of course, due to the fact that recognizable fossils are rarely ever found in rocks older than the basal Cambrian. A third difficulty which one may encounter in attempting to set up even a relative time scale on the basis of fossil data alone is the fact that recognizable index fossils are often lacking in those strata in which one may be particularly interested.

Numerous early attempts to set up absolute time scales for post-Precambrian time were made. In general, the basis of such an estimate was to attempt to determine the rate of accumulation of sediments and then to extrapolate back in time. The length of time represented by each period was calculated on the basis of the maximum known thickness of sediment deposited during a given period. This method obviously contains a number of inherent sources of error. The method is simply a very rigid application of the principle of uniformitarianism. As pointed out by Holmes (1947), such a strict application of uniformitarianism is unwarranted for a number of reasons. Thus, we have no way of knowing whether the rates of sedimentation employed have been constant throughout geologic time. Again, the maximum thickness of sediments found for a given period may not represent the total amount of sediment actually deposited since intervals of non-deposition, or even of erosion, may have occurred from time to time during that period. To illustrate the widely divergent estimates of the elapsed time since the beginning of the Cambrian, based upon rates of sedimentation, Holmes (1947) has prepared the following table.

TABLE I

ESTIMATE OF GEOLOGICAL TIME IN MILLIONS OF YEARS

	Reade (1879)	Walcott (1893)	Goodchild (1897)	Sollas (1900)
Cainozoic	200	2.9	93	4.2
Mesozoic		7.24	237	3.5
Upper Paleozoic	200	17.5	219	5.8
Lower Paleozoic	200		155	4.8
Cambrian to present	600	27.64	704	18.3

A. Winchell (1883) estimated the time from the base of the Cambrian to the present to be about 3 million years, while McGee (1893) concluded that 2400 million years was nearer the truth. Although Reade's estimate of 1879 appears to be in good agreement with the most modern estimates, we find that in 1893, he revised his figure to make 95 million years the entire age of the earth. Holmes (1947) states that "...it is easy to see that Goodchild reached his figures by a lucky but purely accidental combination of low thicknesses with slow rates of deposition."

Other, probably more reliable, attempts to measure absolute time by purely geologic means have been made, but the lengths of time so measured have been generally small compared to the length of time which has elapsed since the Cambrian. Thus, F.J. Pack (Rep. 1934, p. 11) has shown that the wall of Bryce Canyon, Utah, is at present receding at the rate of about two feet per century and that it has receded about one hundred miles since the uplift of the plateau occurred at the beginning of the Miocene. If the present rate of recession does not differ greatly from that during the entire time of recession, his estimate of 26 million years for the length of time since the beginning of the Miocene is probably quite accurate.

The counting of varves is another method which has been used to estimate the length of time required for the deposition of strata. Thus, W.H. Bradley (1930) estimated the duration of the Green River Epoch (Middle Eocene) to be 5-8 million years by counting varves in the lake deposits of the Green River Basin.

However, such opportunities to determine absolute ages by purely geologic means are rare and there is little hope that an absolute time scale will be established by such methods.

The most promising methods by which absolute time scales could be set up to cover long periods of earth history appear to be those based upon the decay of naturally occurring radioactive isotopes. Some excellent review articles on the methods of radioactive age determinations have been published within the past few years; e.g., Faul (1954), Kohman and Saito (1955), Kulp (1955).

Uranium-Lead Methods. The parent element uranium is composed of two isotopes of mass 235 and 238. Each goes through a long radioactive decay scheme containing numerous unstable, radioactive nuclides. The net result of the decay schemes however is as follows:

$$U^{238} \longrightarrow Pb^{206} + 8He^{4}$$
$$U^{235} \longrightarrow Pb^{207} + 7He^{4}$$

When uranium-lead ages are measured, three independent ages may be obtained, these being Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206} ages. The latter is possible because the relative abundances of the two uranium isotopes are constant whereas the decay constants are appreciably different. The extent to which three such ages agree is a good measure of the confidence to be placed in the ages. In a large number of cases, concordancy between the ages has not been obtained. This could be due to a number of things, such as radon leaks (Kulp et al, 1954) and preferential leaching of lead (Collins et al, 1954). However, a significant number of U/Pb ages where excellent agreement has been attained among the three ages are now available and it seems probable that such ages are reliable. Numerous concordant U/Pb ages will be forthcoming in the near future, since mass spectrometric techniques are so rapidly replacing the initial, and less precise, chemical methods of analysis.

An important point to be borne in mind concerning U/Pb ages is the fact that those ages which show concondancy are considered by most workers in the field to be the most reliable determinations of absolute age which we have. Consequently, concordant U/Pb ages are being used to calibrate other methods of radioactive age determination whose decay constants and reliability are less well known. This is being done by utilizing various age determination methods to measure the ages of a number of associated minerals in a single rock unit thought to be well dated by concordant U/Pb ages. This type of work is well illustrated by Aldrich <u>et al</u> (1956) and Wetherill <u>et al</u> (1956). It may well be that concordant U/Pb ages will ultimately provide the basic foundations for the various other methods of age determination.

Other methods of age determination based upon the uranium decay series such as U/He, radiation damage, and total lead methods are discussed in the above reference.

<u>Potassium Methods</u>. One of the isotopes of potassium, K^{40}, is radioactive and decays by beta emission to Ca^{40}, and by K-capture and gamma emission to A^{40}. The most important analytical problem to be solved is the reliable determination of the two decay constants and thus of the branching ratio, that is, the ratio of argon to calcium atoms formed as the result of the decay. Many physical determinations of the branching ratio have been made with values ranging all the way from 0.05 to 1.9. However, recent work seems to support a value of 0.11 for the K^{40} branching ratio (Wetherill <u>et al</u>, 1956, Backus and Strickland, 1955, Moljk, 1955, Ingraham <u>et al</u>, 1950). The work being carried on by Wetherill and his group on micas appears to be very promising and it is probably safe to say that the branching ratio of K^{40} will be known accurately in the near future.

The K^{40}/Ca^{40} decay scheme will probably have only restricted use for age work. This is because we have the least abundant isotope of potassium (0.0119%) decaying to the most abundant isotope of calcium (96.9%). As a result, radiogenic Ca^{40} can be measured accurately only in minerals containing a high concentration of potassium and an extremely low concentration of calcium. K^{40}/Ca^{40} ages then will be restricted to relatively rare minerals such as lepidolite, sylvite and rose muscovite. Backus (1955) has measured the K^{40}/Ca^{40} ages of several lepidolites and compared the ages so obtained with U/Pb, Rb/Sr, and K/A ages of the same mineral or associated ones. He states, "K^{40}/Ca^{40} ages obtained in this research are related to ages obtained by other methods in a discrepant and inconsistent manner. However, the amount of data obtained is not large enough to support any definite conclusions concerning the causes of the discrepancies."

The K^{40}/A^{40} method, on the other hand offers great possibilities. This is because the content of "common" argon in minerals is extremely low and, as a result, any argon present in K-rich minerals is very nearly all of radiogenic origin. It seems quite probable that in the future the K/A method of age determination will be of the utmost usefulness because potassium-rich minerals are common in many materials of geological significance.

Rubidium-Strontium Method. The decay of Rb^{87} to Sr^{87} was first suggested as a possible age method by Goldschmidt (1937), but Ahrens (1949) was the first to attempt establishment of the method by actual experimental work on lepidolites. Ahrens was, however, severely hampered in his attempts for two reasons. These were:

(1) He used the emission spectrograph for the determination of Rb and Sr. Subsequent isotope dilution analyses by Herzog et al (1955) using the mass spectrometer indicated that the accuracy of the optical spectrographic determinations was not of the order necessary for accurate age determinations.

(2) Not having a mass spectrometer at his disposal, and as a result, being unable to determine the isotopic abundances of the Sr contained in the minerals, he was unable to correct for any common Sr that might have been included in the minerals at the time of their formation. This meant that Ahrens was limited to lepidolites for Rb/Sr ages.

Since then, a number of laboratories have been actively engaged in the measurement of Rb/Sr ages, notably Aldrich and his group at the Department of Terrestrial Magnetism and Herzog and his group at M.I.T. Results of age determinations, primarily on the minerals lepidolite, biotite, muscovite and microcline, have been very promising. Some difficulties have been encountered in the determination of the decay constant of Rb^{87}. However, recent work by Aldrich et al (1956) indicates that the half-life of Rb^{87} is very close to 50 billion years. A more detailed analysis of this problem will be given later on in this work.

Although numerous age determinations based upon the various naturally occurring decay schemes have been made, one cannot help but notice the fact that absolute age determinations, in general, have been restricted to only certain types of geological material. In nearly every case the ages have been restricted to such rocks as pegmatites, granites, and volcanics. As a result, until only very recently, the only manner in which absolute age limits could be assigned to the various stratigraphic periods of the earth's history has been through the measured ages of igneous bodies found cutting older sediments or overlain by younger sediments. In most cases only one of the desired relationships was found to be present, that is, either an igneous rock cut older sedimentary strata of known "fossil" age, and a minimum age for the sediments was obtained, or an igneous body was unconformably overlain by sedimentary beds of known "fossil" age, providing a maximum age for the sediments. Rarely, if ever, has there been found a case where, for example, strata known to be uppermost Devonian in age, on paleontologic grounds, are cut by granite or pegmatite containing minerals which may be accurately dated by radioactive methods, which in turn is overlain by sediments known to be lowest Mississippian in age from fossil evidence. If such relationships were common throughout the geologic column, then indeed, absolute age limits could be assigned to the various periods of geologic time. However, as stated above, such relationships are indeed rare or unknown.

It is obvious also that detrital minerals such as biotite, muscovite, or feldspar, commonly found in sediments, could not be used to date the enclosing sediments since such ages would merely represent, at best, the age of the terrain from which they had been transported.

Wickman (1948) suggested a method whereby the absolute ages of certain sediments, mainly limestones, might be measured. This method, now known as the "common strontium method", consisted in measuring the abundance of Sr^{87} in strontium extracted from materials possessing a high ratio Sr/Rb. Wickman felt that as a result of the continuous decay of Rb^{87} to Sr^{87}, the abundance of Sr^{87} should increase with time. Moreover, Wickman suggested that the differences in Sr^{87} abundance would be measurable. Subsequent work by Aldrich <u>et al</u> (1953) at the Department of Terrestrial Magnetism, Herzog <u>et al</u> (1954) at M.I.T., and Gast (1954), failed to disclose the expected variations in Sr^{87} abundances (4% per billion years), and it was concluded that the ratio Sr/Rb in the earth as a whole must be significantly greater than had been assumed by Wickman. Subsequent analyses of the Rb-Sr contents of various terrestrial and cosmic materials support this conclusion. (Herzog and Pinson, 1956).

Ewald <u>et al</u> (1956) have measured the isotopic abundances in Sr extracted from samples of seawater, strontianite, celestite and limestone. In a number of the samples analyzed, they found easily measurable depletions in the abundances of Sr^{87}. Using a value for the ratio Rb^{87}/Sr^{87} of 4.62 (Rankama, 1954), they were able to calculate ages for the various samples. The calculated ages were found to agree quite well with the assumed geological ages of the samples. Their results are shown in Table II.

TABLE II

Sample	Geologic Age	Assumed Age($x10^{-8}$)	Sr^{86}/Sr^{88} (x104)		Sr^{87}/Sr^{88} ($x10^{3}$)		Computed Age $x10^{-8}$	
Seawater	-	-	1195	4	718	3	-	
Strontianite:								
Ascheberg	U.Cret.	1	1194	6	710	2	1.50	.9
Seiseralpe	Permian	2	1196	6	702	4	3.00	1.3
Drensteinfurt	U.Cret.	1	1193	4	709	2	1.59	.9
Celestite:								
Fassatal	Permian	1.5	1193	4	704	1.5	2.53	.8
Agnedotte	Tertiary	0.5	1192	4	709	2	1.68	.9
Jena	Triassic	1.5	1194	4	702	3	2.92	1.1
Brown County	?	?	1194	4	711	2	1.31	.9
Limestone:								
Schwingen	Cambrian	5	1195	5	692	2	4.86	.9
Wirbelau	M.Devonian	3.3	1196	6	702	3	3.001	.1

The inability of other workers to find such variations in the abundances of Sr^{87} cannot be explained at this time. Thus, we have analyzed seawater strontium and found the abundances of

Sr^{87} to be .0702. Although Ewald's results are extremely encouraging, if reproducible, the high errors assigned to the ages calculated indicate that further refinements in instrumentation and techniques will be necessary before sufficiently accurate ages will be obtainable from common strontium isotope abundance measurements.

The most direct approach to the problem of measuring the absolute ages of sedimentary rocks would be to find some mineral which occurred in sedimentary rocks and which formed at the time of deposition of the sediments or very shortly thereafter. This mineral would also have to possess a number of other characteristics. These are:

(a). It should contain enough of the parent element to give rise to measurable amounts of the daughter element.

(b). It should preferably be a mineral that was common, not only geographically but also stratigraphically.

(c). It should be a mineral which was stable, that is, one which would remain a closed system with respect to either ingress or egress of daughter or parent element during geological time.

(d). It should be a mineral whose physical properties will allow a clean separation to be made of the mineral from associated materials.

If one examines the minerals found in sedimentary rocks, which are thought to be authigenic, with the objective of measuring absolute ages by radioactivity methods, the mineral glauconite immediately presents itself. Glauconite, since it contains potassium as a major element, should lend itself to either Rb/Sr or K/A age determinations. The probable applicability of the Rb/Sr method follows from the fact that because of their similar properties, potassium and rubidium follow one another very closely geochemically, and an enrichment in one implies an enrichment in the other.

K/A glauconite age measurements have already been attempted by others, e.g., Lipson (1956), Wasserburg and Hayden (1955). Their results will be reported on later in this work. The research reported on here was undertaken with the objective of finding out whether or not Rb/Sr ages of glauconite samples could be used as an aid in setting up an absolute time scale for the sedimentary rocks.

CHAPTER I

BACKGROUND MATERIAL

Geochemistry of Sr and Rb. Rubidium is an alkali metal element, whereas strontium is a member of the alkaline earth group of elements. The geochemistry of these two elements has been studied extensively by Ahrens (1949, 1947, 1951a, 1951b), Pinson (1952), Goldschmidt (1954), and Rankama and Sahama (1950). The treatment given here will necessarily be very brief, but, it is hoped, will serve to bring out the main factors necessary for an understanding of the behaviour of these two elements in the crust of the earth.

Rubidium has an ionic radius of 1.44A. Potassium has an ionic radius of 1.33A. If Goldschmidt's rules apply, then we should expect Rb to follow K geochemically since the difference in their radii is less than 15% of the larger and since both elements are well screened, that is, both have low ionization potentials. This is indeed found to be the case. There exists a very striking relationship between the contents of K and Rb in most crustal rocks (Ahrens and Pinson, 1951). The ratio K/Rb is found to be 220 ± 50 (Herzog et al, 1956) for the common rocks of the crust, e.g., basalt, granite, diorite, etc., and what seems to be even more striking, this relationship also appears to be true in the case of the chondritic meteorites (Ahrens and Pinson, 1951). The approximately constant relationship between potassium and rubidium contents however, does appear to break down in the case of those rocks representing the very latest stages of magmatic crystallization, notably the pegmatites. In these rock types, rubidium appears to be enriched relative to potassium. This is also true of the minerals biotite and muscovite in the common igneous rocks. Rubidium is greatly depleted relative to potassium in achondrites and sylvites.

The fact that rubidium tends to be enriched relative to potassium during the latest stages of magmatic crystallization would seem to indicate that during the crystallization of the main body of the magma, potassium was preferred over rubidium at the sites of crystal formation. The liquid phase would then tend to become enriched in rubidium. This again is in accordance with the rules of ionic crystallization set up by Goldschmidt, since of two elements competing for a crystal site, that possessing the higher charge-to-radius ratio will be preferred.

Strontium on the other hand is divalent. It has an ionic radius of 1.18A and tends to follow calcium which has an ionic radius of 1.01A in much the same fashion as rubidium follows potassium. Geochemical coherence between these two elements, however, is not nearly as close as that between potassium and rubidium. However, since the difference in their ionic radii is less than 15% of the larger, the two elements do follow one another quite closely. As a result, strontium tends to be concentrated in calcium-rich minerals and rocks such as the plagioclase feldspars and limestones. However, as a result of its similarity in size to potassium, strontium shows a significant concentration in the potash feldspars as well. Due to the depletion of strontium during the main sequence of crystallization, the late residual liquids from which the pegmatitic minerals are thought to form contain very little strontium.

In the light of the above observations then, two opposing trends are seen to be in operation, concentration of rubidium and depletion of strontium in the late stage crystallates. The result is that rubidium bearing minerals of pegmatites, notably lepidolite, biotite, muscovite, and microcline, are particularly suited for Rb/Sr age determinations. The extremely low concentrations of normal strontium in such minerals allows radiogenic strontium to be measured very accurately. This is well illustrated in the case of the Bikita Quarry lepidolite, which was found to contain less than 1% , the strontium present being almost entirely radiogenic Sr^{87}.

Recent work by Herzog et al (1956) at M.I.T. and Aldrich et al (1956) at the Department of Terrestrial Magnetism has shown that biotite and muscovite separated from such common igneous rocks as granite, diorite, and diabase, are suitable for Rb/Sr age determinations since, here also, the common strontium content is low, of the order of a few parts per million. These observations are of great importance since they indicate that Rb/Sr age determinations will not be limited to the relatively rare pegmatitic minerals. Table III shows more or less typical abundances of strontium and rubidium in various crustal and cosmic materials.

TABLE III

Material	Normal Sr	Radiogenic Sr	Rb
Lepidolite, Bikita Quarry, So. Rhodesia	0	329	9170
Biotite, Stone Mt., Georgia, U.S.A.	7.14	1.19	1120
Muscovite, Stone Mt., Georgia, U.S.A.	10.34	1.24	1125
Orthoclase, Conway Granite, N.H.	103	.23	583
G-1 Granite, Westerly, R.I.	233	-	216
W-1 Diabase, Centreville, Va.	177	-	28.5
Sea Water	7.2	-	.12
Homestead Chondrite	11.9	.04	4.0
Forest City Chondrite	16.0	-	4.3

All analyses given in p.p.m.; all analyses are isotope dilution analyses made at M.I.T.

With regard to the relative abundances of strontium and rubidium in the crust as a whole, mass spectrometric investigations of the abundance of Sr^{87} in common strontium extracted from materials possessing a high ratio Sr/Rb and of widely different geologic ages seems to indicate a ratio Sr/Rb of about 5/1. If the results reported by Ewald <u>et al</u> (1956) (see pp. 10-11 this work) can be confirmed by other laboratories however, the ratio Sr/Rb in the crust as a whole is probably closer to 1/1.

The half-life of Rb^{87}. If accurate absolute age determinations are to be made utilizing the decay of Rb^{87} to Sr^{87}, it is imperative that the decay constant of Rb^{87} be known accurately. Evidence of beta decay in rubidium was first reported by Thompson (1905). The fact that Rb^{87} was the active isotope was shown by Hemmendinger and Smythe (1937) and by Hahn, Strassman and Walling (1937). Hemmendinger and Smythe, using a high intensity mass spectrometer, with a sample of rubidium, collected separately the masses from 84 to 90. They found that the activity of all other masses was negligible as compared to that of the mass 87 fraction. Hahn, Strassman and Walling took an entirely different path. They obtained a rubidium rich mica from Manitoba and separated a strontium concentrate from it. This was analysed mass-spectrographically by J. Mattauch. The photographic plate showed a strong line at mass 87, while no lines were present for masses 84, 86 and 88.

Since that time, numerous determinations of the activity of Rb^{87} have been made. Two general methods have been employed:

(a) Direct measurement with counters

(b) Indirect measurements where the concentrations of radiogenic strontium and Rb^{87} in a mineral are measured, and the half-life which would be necessary to give the correct age of the mineral is calculated. The correct ages of the minerals were determined by either concordant U/Pb ages or through purely geological methods. Table IV lists some published values of the half-life.

TABLE IV

Investigator	T1/2	d/min./mg.Rb	Method
Strassman and Walling (1938)	6.3 x 10^{10}	-	Geological
Haxel, Houtermans and Kemmerich(1948)	5.95	43.5	4 π G-M counter
Kemmerich(1949)	4.10	63.1	Screen-wall G-M counter
Curran, Dixon and Wilson (1951)	6.41	40.4	Screen-wall proportional counter
MacGregor and Wiedenbeck Wiedenbeck (1952)	6.37	40.6	4 π G-M counter
Lewis (1952)	5.93	43.7	Scintillation spectrometer
Geese-Bahnisch and Huster (1954)	4.30	60.1	4 π G-M counter

A considerable spread in the values obtained is shown in Table IV. A great deal of difficulty is experienced in measuring the activity of rubidium as a result of the unusual distribution of the energy of the electrons emitted. Thus, the maximum energy of the spectrum is 275kev while the average energy is about 45kev. Details of the shape of the spectrum at low energies are difficult to deduce.

Recently, Aldrich <u>et al</u> (1956) have announced extremely encouraging results in an effort to determine the rubidium half-life accurately by the indirect or geological method. Aldrich and his co-workers first measured the ratio, radiogenic Sr^{87}/Rb^{87}, for eight rubidium rich minerals from the Brown Derby pegmatite, Gunnison County, Colorado. The results of these analyses are shown in Table V.

TABLE V

Mineral	Rb		Radiogenic Sr		Radiogenic Sr^{87}/Rb^{87}
Muscovite	1870	50	36.5	1	.0195
Microcline	2690	100	48.7	1	.0181
Lepidolite (coarse bk.)	5550	200	110	3	.0198
Lepidolite (med. grain)	5570	200	121	3	.0210
Lepidolite (med. grain)	5570	200	114	3	.0195
Lepidolite (fine grain)	5890	200	130	3	.0220
Lepidolite (white)	6130	200	118	3	.0192
Lepidolite (coarse)	6870	200	134	3	.0195

All values given in p.p.m.

The values of the ratio radiogenic Sr^{87}/Rb^{87} are seen to be constant for these eight samples within the stated limits of error. This would indicate that the measured ratio is independent of the mineral used, and that Rb-rich minerals in pegmatites are formed at approximately the same time. Aldrich then measured the Pb^{206}/U^{238} and Pb^{207}/U^{235} ages of five uraninites ranging in age from 375 million years to 1800 million years. In all cases the U/Pb ages were found to be concordant. Rb-rich minerals from the same rock units were then analysed for their radiogenic Sr^{87}-Rb^{87} contents. In each case, the half-life which would be necessary for the Rb decay in order that the Rb/Sr ages agree with the concordant U/Pb ages was calculated. The results are shown in Table VI.

The agreement between the calculated half-lives for the Rb^{87} decay is indeed striking and gives a mean value of $5.0 \pm 0.2 \times 10^{10}$ years. The only assumption made is that the uranium bearing minerals and the rubidium bearing minerals were formed at very nearly the same time. This assumption appears to have been justified in the light of the results obtained. Numerous Rb/Sr age determinations by the M.I.T. group support a value for the Rb^{87} half-life of about 5.0×10^{10} years. For these reasons, this value of the Rb half-life has been used in the work reported on here.

TABLE VI

Pegmatite Location	U/Pb Ages (10^6 yr. units)			Rb/Sr Data		T1/2
	Mineral	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Mineral	Sr^{87}/Rb^{87}	
Bikita Quarry, So. Rhodesia	Monazite	2640 ± 100	2680 ± 100	Lepidolite	0.0380 ± .001	5.0
Viking Lake Saskatchewan	Uraninite	1790 ± 50	1830 ± 50	Biotite	0.0270 ± .001	4.8
Bob Ingersoll, Keystone, S.D.	Uraninite	1580 ± 30	1600 ± 30	Lepidolite	0.0239 ± .001	
				Muscovite	0.0244 ± .001	4.8
				Microcline	0.0224 ± .001	
Cardiff Twsp., Ontario	Uraninite	1020 ± 20	1020 ± 20	Biotite	0.0140 ± .0007	5.1
Fission Mine, Wilberforce, Ont.	Uraninite	1040 ± 20	1050 ± 20	Biotite	0.0140 ± .0007	5.2
Spruce Pine, N.C.	Uraninite	375 ± 10	380 ± 10	Muscovite	0.00515 ±.0002	5.0
				Microcline	0.00535 ±.0002	

CHAPTER II

THE MINERAL GLAUCONITE

Occurrence. Glauconite bearing sediments have been recognized in nearly all of the periods of geologic time from the Cambrian up to the present. Glauconite is being formed today on practically all of the stable continental shelf areas of the world, and glauconitic sediments of Cambrian, Ordovician, Silurian, Devonian, Mississippian, Permian, Jurassic, Cretaceous, and Tertiary age are known. It seems probable that glauconitic sediments will also be found in strata of Pennsylvanian and Triassic age somewhere in the world. Glauconitic sediments are abundant in strata of Cambrian and Cretaceous age. No occurrences of glauconite definitely known to be Precambrian in age have been reported, although two cases of possibly Precambrian glauconites are known to the author. One is from the Murray shale member of the Chilhowee Group of Tennessee, where glauconite occurs 500' stratigraphically below the lowest recognizable Cambrian fossil. A very similar occurrence has been reported on Ella Island, northeast Greenland (Schaub, 1955). Here again, the glauconitic horizon is located some 500' below the first fossiliferous Lower Cambrian beds. Two reasons have been advanced to explain the apparent absence of glauconite in beds of Precambrian age. They are:

(a) Glauconite was formed during the Precambrian but was later destroyed by metamorphism.

(b) Glauconite requires the presence of decaying organic material in order to form and such material was lacking in the Precambrian.

It is difficult to say whether ~~either~~ or not either or both of these hypotheses are correct. Certainly the evidence seems to favor the conclusion that considerable life did exist in the seas, at least during the later stages of the Precambrian. Otherwise, it would be extremely difficult to explain the sudden appearance of highly developed organisms at the beginning of Cambrian time. It is also true that much of the Precambrian terrain exposed today has undergone intense metamorphism which could quite conceivably lead to the alteration and disappearance of glauconite as such. The reason for the apparent lack of glauconite in strata of Precambrian age must, for the present, remain unanswered.

Environment of formation. Cloud (1955) has summarized, in excellent fashion, the conclusions reached by many of those who have studied glauconite with a view to determining the type of environment in which the mineral forms. His conclusions are given below:

1. Stratigraphic range -- Cambrian to present.
2. Present areal distribution -- 65 degrees south to 80 degrees north, off most oceanic coasts and mainly on the continental shelves away from large streams.
3. Salinity -- known to originate only in marine waters of normal salinity. Although it theoretically might form in

potassium rich saline lakes, it is not known to occur in salt lakes or in fresh water deposits.

4. Oxygenation -- formation requires at least slightly reducing conditions (at sites of origin within the enclosing sediments, if not the bottom waters).
5. Organic content of bottom sediments -- formation is facilitated by the presence of decaying organic matter, which results in reducing conditions. Bottom habitat favorable to sediment ingesting organisms with low oxygen requirements.
6. Depth -- mainly neritic; moderate to shallow, but yet appreciable depth suggested. Rare in sediments below 1000 and above 5 fathoms, uncommon above 10 and below 400 fathoms, and formation favored in upper part of 10 to 400 fathom interval.
7. Temperature -- tolerance apparently wide but formation probably not favored by markedly warm waters. Although geographic range is from polar to tropic regions, tropical glauconite seems so far to be recorded wholly in the cooler waters below 30 fathoms, and mainly below 130 fathoms.
8. Turbulence -- no intrinsic requirements. Although evidence of turbulence is commonly found in associated sediments, continued marked turbulence would seem incompatible with conclusion 4.
9. Source material -- micaceous minerals or bottom muds of high iron content.

10. Sedimentary influx -- Probably slight. Preferably just enough to supply needed mother elements. Formation favored on continental shelves, swells, or banks off the coasts of crystalline land areas that lack important rivers.

11. Associated sediments and organic remains -- found mainly in calcareous, detrital sediments and impure granular limestones. Rare in pure clay rocks, pure quartz sandstone, or chemically precipitated carbonates. Commonly associated with remains and fecal pellets of sediment ingesting organisms or as internal fillings of Foraminifera. Rare in or absent from beds that are rich in algae, corals, or bryozoans, and probably reworked or transported where so found.

Physical properties of glauconite. Glauconite varies in color from yellow-green through grass-green to a very dark blue-green, almost black. The mineral has a specific gravity which varies from 2.2 to 2.8. It is moderately magnetic. Cleavage, when present, is micaceous. Individual crystals of the mineral are rarely seen, the grains generally being composed of an aggregate of very minute crystals. The grains are generally smoothly rounded, often elongate and somewhat curled in shape. Glauconite grains quite often form perfect casts of forams and other shelled creatures. Indeed, the early investigators concluded that glauconite could form only within shells (Murray and Renard, 1891; Collet and Lee, 1906).

Ross (1926) has determined the optical properties of glauconite. He wrote:

> "The indices of refraction of glauconite .... are a = 1.597, b = 1.618, c = 1.619, c-a = .022 ± .003. Optical character negative (-). The acute besectrix is nearly but not quite normal to the cleavage. X is inclined to C about 3°. The adsorption is Z = Y > X; pleichroism Z and Y are yellow, X dark bluish green. The optical angle is nearly constant with 2V = 20°, 2E = 33°. The dispersion is distinct but the adsorption of the red by the blue-green mineral makes it difficult to observe."

Chemical composition. Glauconite is principally a hydrous silicate of iron, aluminum, and potassium. Although investigators are not in complete agreement as to the chemical formula of glauconite, they do not disagree very markedly. The formulae set up by four investigators will be given here.

Hallimond (1922) proposed that the formula of glauconite could best be expressed as:

$$R_2O.4(R_2O_3,RO).10SiO_2.nH_2O$$

The alkalies are represented by R_2O, ferric iron and alumina by R_2O_3 and ferrous iron and magnesium by RO.

Ross (1926) concluded that glauconite represented an isomorphous series, the two end-members being represented by the following:

$$2H_2O.K_2O.(MgO,Fe''O).2(Fe_2^{'''}O_3, Al_2O_3).10SiO_2\ 3H_2O$$

$$2H_2O.K_2O.(MgO,Fe''O).3(Fe_2^{'''}O_3,Al_2O_3).10SiO_2\ 3H_2O$$

Schneider (1927) concluded that the composition of glauconite could best be represented by the formula:

$$(K,Na)(Fe'',Mg)(Fe''',Al)_3Si_6O_{18}\cdot 3H_2O$$

Schneider found the greatest variation to be in the ferric iron and alumina contents, alumina ranging from a high of 10% to almost zero. Soda is sometimes present to the extent of 2% but only rarely is it nearly equal to potassium. Table VII represents the average of 14 glauconite analyses as given by Schneider. No difference in composition could be found between ancient and recent glauconites.

TABLE VII

SiO_2	49.0
Al_2O_3	7.7
Fe_2O_3	21.2
FeO	2.8
MgO	3.4
CaO	.1
Na_2O	1.0
K_2O	6.8
H_2O	7.8
	99.8%

Gruner (1935) averaged the analyses used by each of the above three investigators. He states, "They are remarkably similar. It would be difficult to say which (formula) is closest to the truth. They bear out the contention that glauconite is a definite species." Gruner's formula for glauconite is:

$$OH_{6-10} \cdot K_{2-3}(Mg, Fe'', Ca)_{1-3}(Fe''', AlSi)_{3-6}(Si_{13-14}Al_{2-3})O_{38-40}$$

Structural composition. Structurally, glauconite is a mica. The micas in general are composed of a number of discrete structural units which are repetitive. One such unit consists of a sheet of silica tetrahedrons, each tetrahedron sharing three oxygens, these shared oxygens being co-planar. A second structural unit found in the micas is composed of aluminum or magnesium ions octahedrally coordinated by O'' or OH', depending upon charge balance requirements. In the micas, an octahedrally coordinated sheet of Al and/or Mg ions is sandwiched between two sheets composed of silica tetrahedrons. The "apex oxygens" of the tetrahedral sheets are shared with the intervening octrahedral sheet. These "sandwiches" extend indefinitely in the a and b directions and are stacked, one atop another, in the c direction. Interlayers of K, Na and Ca ions are present between each "sandwich" in order to maintain charge balance. The number of such interlayer cations will depend upon the charge deficiences which exist within the tetrahedron-octahedron-tetrahedron units.

Muscovite is known as a dioctahedral mica, i.e., only two-thirds of the octahedral positions are filled, and the cations in the octahedral sheets are all aluminum ions. Biotite, on the other hand, is trioctahedral. Here, the octahedral sheets are populated by divalent Fe and Mg ions. In some cases, trivalent iron is also present. In the case where octahedral positions are filled largely by divalent ions, all or nearly all of the possible octahedral sites will be filled. Grim (1953) states that "glauconite is a dioctahedral illite with considerable replacement of Al ''' by Fe''', Fe'' and Mg''." It appears that, in many cases, even less than two-thirds of the possible octahedral positions are filled. As a result, there is a charge deficiency within the octahedral as well as the tetrahedral layers. The interlayer cations of Na,K, and Ca appear to balance these deficiencies.

Mode of origin. Numerous theories have been advanced to explain how the mineral glauconite is formed. The entire question of how, and from what, glauconite forms is an extremely important one from the viewpoint of one interested in measuring the absolute ages of glauconite. Thus, if glauconite simply represents an alteration product of some detrital mineral, such as biotite, erroneous ages might be obtained. This springs from the fact that in any mineral which is to be used to determine absolute ages, the concentration of daughter element present must be limited to that formed since the formation of the mineral itself. To illustrate, let us suppose that a biotite of Precambrian age was deposited in a Devonian sea and was subsequently altered to glauconite. Unless the radiogenic Sr already present in the biotite at the time of its deposition was entirely removed during the process of glauconization, an erroneous Rb/Sr age would be obtained for the Devonian strata in which the glauconite was found. The importance of the manner of formation of the mineral is then obvious.

One of the most widely publicized theories of glauconite formation is that advanced by Galliher (1935), who studied bottom samples from Monterey Bay, California. He found that biotite was being altered to glauconite, and implied that all glauconite formed as the result of biotite alteration. Galliher found that:

(a) Glauconitic sediments were the off-shore equivalents of those containing biotite.

(b) The alteration of biotite to glauconite included oxidation of its iron, retention of potash, hydration, partial loss of alumina, and swelling and cracking of the biotite.

(c) The alteration of the biotite is started in the sulfuretum (the black mud environment) produced by sulfur bacteria.

(d) Near shore mica was brown, with but little green mica. As the distance from shore increased, the proportion of green mica with respect to brown mica increased.

(e) When the glauconite zone is reached, the percentage of glauconite increases as the percentage of mica decreases.

All stages of fresh, brown mica to glauconite were observed, and Galliher supports his observations with excellent photomicrographs. The succession of events observed in the alteration went as follows: brown mica to green mica; hydration and swelling along cleavage planes; light green, powdery glauconite along cleavage planes; cracking across cleavage planes and development of glauconite; irregularly shaped grains composed entirely of glauconite; smoothing and rounding of grains. Galliher was also able to trace the changes in optical properties for the various stages of the series.

It would appear from the evidence given by Galliher that glauconite is undoubtedly forming as a result of the alteration of biotite in Monterey Bay, California. However, the conclusion that all glauconite, past and present, has been formed through the alteration of biotite, which he seems to draw, is certainly not warranted. The extensive glauconite deposits of Maryland and New Jersey could not be explained in this manner. It would be necessary to have great thicknesses of almost pure biotite deposited during the Cretaceous and early Tertiary, a highly unlikely occurrence. Biotite in these deposits is extremely rare. Again, the writer has separated some thirty specimens of glauconite from rocks of all types and ages and in nearly every case, no biotite whatsoever was noted in association with the glauconite. In two or three cases where it was found, it was extremely rare and showed no tendency to alter to glauconite. It should also be remembered that biotite is an unstable mineral, and under conditions of weathering and erosion, soon breaks down. As a result, biotite in significant quantities is rare in sedimentary rocks. Muscovite, on the other hand, is much more stable and is the common detrital mica found in sediments.

Takhashi and Yagi (1929) have studied glauconitic bottom sediments from the sea of Japan. They found that mud pellets, which they concluded were fecal pellets, composed of fine clay for the most part, were in the process of being altered to glauconite. All stages, from the completely unaltered, grey, pellets to completely glauconitized green pellets were observed. Chemical analyses indicated that in the process, the potassium content increased sharply, as did the ferric iron content, whereas the concentration of alumina fell.

Ehrenberg (1855) and Pourtales (1869), noting the occurrence of glauconite within the shells of marine animals, concluded that glauconite was formed inside such shells as a result of chemical reactions influenced by the decaying animal matter. Later investigators have found, however, that most glauconite has not been formed in shells but rather, in some cases, glauconite was washed into the shells.

Light (1950, 1952), after studying some 150 samples of glauconite from the New Jersey coastal plain, concluded that the parent material of the glauconite was the associated illitic clay. The distinct similarity in composition and structure between glauconite and the illitic clay minerals has been shown by Grim (1953). Light also noted that where glauconite was definitely authigenic, it was invariably associated with illite. This correlation was not necessarily true, however, in those cases where the glauconite was thought to have been transported from elsewhere.

Hendricks and Ross (1941), in considering the genesis of glauconite, state that: "The improbability of derivation from a material carrying adequate potassium and the invariable formation under a marine environment, indicates that potassium was derived from the sea, and the same is, no doubt, true of magnesium." They also state: "The near constancy in the magnesia content of the glauconites reflects the essentially unchanging nature of the environment and the structural requirements of the mineral lattice. The other constituents of glauconite, silicon, aluminum, and iron could be supplied adequately by any mud."

Grim (1955) states that montmorillonite appears to be forming today in areas undergoing chemical weathering and erosion. Illite, on the other hand, does not appear to be formed under such conditions, but rather breaks down under conditions of chemical weathering. In the stratigraphic column, on the other hand, clays are generally illitic, montmorillonite being confined to volcanic ash beds. Grim believes that originally the clays found in the stratigraphic column were deposited as montmorillonite and were subsequently altered to illitic types through adsorption of potassium from sea water.

It seems possible that, in the light of Grim's remarks, glauconite may also represent an alteration of montmorillonitic clays as a result of their contact with sea water. The illitic clays are very similar in structure and composition to glauconite. Indeed Grim (1953) states that glauconite is a dioctahedral illite. If glauconite then represents simply one form of illite, its mode of formation would be attractive for a number of reasons. These are :

(a) Glauconite and illite are distinctly similar in chemical and structural composition. Their similarity in chemical composition is shown in Table VIII below. The glauconite analysis represents an average of 14 analyses taken from Schneider (1927). The illite analysis is an average of two analyses taken from Grim (1955).

(b) If Grim's theory, that the illitic clays found in the sedimentary column were originally deposited as montmorillonite, is correct, and glauconite merely represents a special type of illite, then the probability is that any radiogenic Sr found in such a glauconite would represent the decay of rubidium only since the time of formation of the glauconite, that is, shortly after the deposition of the montmorillonitic clays.

(c) Since montmorillonite and illitic clays are common constituents of sediments, an ample supply of parent material for glauconite formation would be available.

(d) Clay minerals have been observed altering to glauconite, or intimately associated with it, by a number of investigators, e.g., Light (1952, 1950), Ichimira (1940), Takahashi and Yagi (1929).

In summary, the evidence seems to suggest that glauconite may form as the result of alteration of a number of minerals, generally micas or mica-like minerals. There is evidence to support the theory that glauconite can be formed through alteration of illitic or montmorillonitic clay minerals in contact with sea water. This latter theory is particularly attractive to one interested in using glauconite for Rb/Sr age determinations since, if the theory is correct, the amounts of daughter element present in glauconite probably represents only that produced from the time of formation of the glauconite. However, if the glauconite used for Rb/Sr age determinations were simply an alteration product of some pre-existing, detrital, potassium rich mineral, such as biotite, muscovite, or feldspar, the possibility of incomplete removal of radiogenic strontium, formed previous to transport and deposition of the mineral, as a result of the alteration to glauconite, would be present. This could lead to measured ages which would be too old.

TABLE VIII

	Glauconite	Illite
SiO_2 - - - - - - - -	49.0	51.4
Al_2O_3 - - - - - - -	7.7	25.1
Fe_2O_3 - - - - - - -	21.2	4.9
FeO - - - - - - - -	2.8	1.3
MgO - - - - - - - -	3.4	3.3
CaO - - - - - - - -	.1	.2
Na_2O - - - - - - - -	1.0	.1
K_2O - - - - - - - -	6.8	6.4
H_2O - - - - - - - -	7.8	7.3

CHAPTER III

MASS SPECTROMETRY

General description of mass spectrometer. The mass spectrometer is an instrument which splits a single beam of ions composed of different masses into a number of beams, each of the resulting beams representing a single mass/charge ratio. Thus, if an element composed of more than a single isotope is ionized, beams composed of each of the isotopes making up that element may be formed. The relative intensities of these beams are equal to the relative proportions of the isotopes present, provided that no mass discriminations are introduced. Excellent articles on the theory of mass spectrometry are available, e.g., Inghram and Hayden (1954), Barnard (1953).

The mass spectrometer in general consists of: (1) a source for the production of ions; (2) a high voltage supply for "drawing out" and accelerating the ions; (3) a collimating system; (4) a magnetic field to split the beam into a number of beams each composed of ions possessing a single mass/charge ratio; (5) a collector and amplifier; (6) a recorder.

The instrument used in this research was a Nier type, 60° sector, 6 inch radius, direction focussing mass spectrometer. This type instrument has been fully described by Nier (1947). The method of production of positive ions used was thermionic emission. Strontium was placed on the filament in the form of strontium oxalate (SrC_2O_4), while rubidium was put on either as the sulfate or nitrate. All of these compounds, at elevated temperatures, are converted to the oxide. After conversion to the oxide, further heating of the filament results in evaporation of the oxide. Some of the strontium and rubidium atoms are ionized and these form the ion beam. The filament was enclosed by a tantalum metal box with a wide slit in its top, this slit being co-linear with, and lying just above, the filament. The filament and box were insulated from one another but were at the same potential, about 800 volts negative. The box could be made positive or negative, relative to the filament, by means of a battery. The difference in potential between box and filament was variable from 0 to 22½ volts, either positive or negative. This serves to change the shape of the drawing out field in order that the maximum number of ions from the region around the filament may be pulled out through the box slit.

The drawing out field can be thought of as the valley which would appear if equipotential lines were drawn in the filament region and down which the positive ions tend to move. By varying the potential of the box relative to the filament, the shape of this valley is changed, and more or less ions may be drawn out depending upon the position of the sample on the filament, the degree of alignment between the filament and the box slit, the shape of the filament (flat, bowed up, bowed down, wrinkled, etc.), and the distance between filament and box.

After the ions have moved outside the box, they pass between two half plates or split-plates. The split-plates are insulated from one another and from the box and filament. Both plates are at the same potential, generally about 2500 volts negative. This high potential is the accelerating voltage and gives the ions a high velocity. The rapidly moving ions then pass through two collimating slits and the resulting beam moves down the tube of the mass spectrometer. By means of a battery, one of the two split-plates can be given a slightly higher or lower potential than the other, enabling the beam to be deflected for focussing purposes.

The beam is now moving down the tube and is a composite beam, that is, it is composed of ions of different mass. The beam then passes through a sectored magnetic field of 6" radius and about 4000 gauss. Since ions are charged particles, they are deflected by the magnetic field, the amount of deflection of a given ion being dependant upon its mass/charge ratio and also upon its kinetic energy or velocity. Since the ions in the beam are essentially mono-energetic, the composite beam which entered the field is split into a number of beams, each representing a particular mass/charge ratio. These beams then move on up the tube to the collector.

The collector consists of a nichrome metal cup with a slit in its top. The width of this slit is such that only one beam may pass through it at any given instant. The beam falling on the slit strikes a collector plate. The resulting current is put across a 10^{11} ohm Victoreen resistor, amplified by a vibrating reed electrometer, and fed to a Weston or Brown strip chart recording potentiometer. The different ion beams are made to pass in succession across the slit of the collector, and onto the collector plate, by automatically varying the strength of the magnetic field, first in one direction and then the other, across the mass range desired.

In order that good resolution of the ion beams be attained, it is necessary that the mean free path of the ions be approximately twice the distance travelled by the ions from the ion source to the collector. It is thus necessary to maintain within the system a vacuum of approximately 1 x 10^{-6} mm. of mercury. This is accomplished with the aid of a Welch duo-seal forepump, a mercury diffusion pump designed by Homer Priest of M.I.T., and a cold trap. Pressures of 2 x 10^{-5} mm. were attained with dry ice on the cold trap within two hours of mounting the sample. It was found that rubidium could be run at such pressures. However, with liquid nitrogen on the cold trap, the pressure would immediately fall to 5 x 10^{-6} mm. so that this was done for every run. In the case of common strontium isotope ratio runs, pressures of at least 2 x 10^{-6} mm. were found to be necessary in order that acceptable resolution be attained. Such pressures were attainable within three hours of placing the sample on the filament. However, outgassing of the sample as the filament was heated up to a temperature where strontium ions would be formed resulted in the pressure rising to about 2 x 10^{-5} mm. and it required about three hours of further pumping to restore the pressure to 2 x 10^{-6} mm.

Methods of positive ion production. There are a number of methods now in use whereby positive ions may be produced. Where the element to be ionized can be introduced as a gas at room temperatures, the problem is greatly simplified, and the gas is simply streamed through a beam of electrons produced by an electron gun. In the case of other elements which cannot be conveniently introduced as gases, either in the elemental state or in compound form, the sample must be placed in the mass spectrometer as a solid or liquid on a filament. This is true of the elements analysed in this research, strontium and rubidium. When the sample to be ionized is non-gaseous at room temperatures, there are two general methods of ionization:

(a) The sample can be heated and evaporated from a filament or crucible, and the vapor thus obtained ionized by electron bombardment.

(b) Atoms of the sample can be ionized through simple heating, that is, by thermal ionization.

Thermal ionization may be brought about in two ways; the sample may be ionized by strongly heating a single filament, the filament upon which the sample was placed, or the sample may first be evaporated from the sample filament and then atoms or molecules of the sample vapor may be ionized by striking a second, much hotter, ionizing filament placed somewhere else in the vicinity of the sample filament.

Electron bombardment of vapors was not attempted in this work. However, the two methods of thermal ionization cited above were tried. For the major portion of the work reported here, ions were obtained by thermal ionization from a single filament. Rubidium ionizes at a much lower temperature than does strontium. It was particularly desirable to have strontium in the oxide form as this compound is very refractory. If this were not so, strontium samples would have evaporated completely from the filament before temperatures high enough to cause ionization of the strontium were attained.

An attempt was made to utilize a double filament source in which the sample was placed on an evaporating filament and the vaporized particles were ionized by striking a second, ionizing filament. It was thought that fractionation effects could be minimized by ionizing molecules of some strontium compound, rather than atoms of strontium. This follows from the fact that the degree of isotope fractionation during thermionic emission is thought to be proportional to the square root of the mass ratio of the two atoms or molecules involved. It was decided to place the strontium on the sample filament as strontium iodide (SrI_2), a compound which could be easily vaporized. It was predicted by Inghram and Hayden (1954) that strontium iodide molecules would be driven off the sample filament. Some of these molecules would then strike the much hotter, ionizing, filament and be ionized to SrI^+. The molecular weight of a SrI^+ ion, in which the strontium was of mass 88, would then be 215, while that of an ion containing strontium of mass 84 would be 211. Iodine itself is composed of only one naturally occurring isotope so that no difficulties were anticipated on that score. The square root of the mass ratio, then, for SrI^+ ions composed of strontium of mass 88 and mass 84 would be equal to 1.009. In the case where Sr^+ ions are used, on the other hand, the square root of the mass ratio would have a value of 1.024 for the 88 and 84 isotopes. We should then expect fractionation effects to be cut by a factor of about 2.5 when the iodide was used. However, this was not to be.

An ionizing filament was constructed and placed in the source along with the sample filament. SrI_2 was placed on the sample filament and vaporized. The ionizing filament was run at a high temperature. However, no SrI^+ ions were obtained, only Sr^+ ions. Apparently the reaction $SrI_2 \longrightarrow Sr + I_2$ occurred before sufficient temperatures were attained to vaporize SrI_2. This had been predicted by G. MacDonald, of this department.

Another reason for the work with the double filament source was to attempt to improve sensitivity. A double filament source possesses the advantage that the temperature of the sample (evaporating) filament can be varied independently of the ionizing filament temperature. Thus, the sample may be vaporized at a slower rate while the ionizing filament is kept at the maximum temperature possible. It was hoped that in this fashion, a greater efficiency of ionization for strontium might be attainable. Although easily measurable strontium ion currents were generated using this type source, no increase in sensitivity was observed, and since the method was unable to diminish fractionation effects, it was abandoned in favor of the simpler, single filament source.

A brief description of the double filament source constructed, however, is as follows. The filament already present in the single filament sources used in this laboratory was employed as a sample or evaporating filament. This was a tantalum ribbon filament, 0.001" x 0.030" x 0.5". A second, ionizing, filament was added so that it was parallel to and just above the sample filament. The ionizing filament was constructed of 0.003" tungsten or molybdenum wire. Each filament was heated with an independent alternating current filament supply.

The method of isotope dilution. One of the greatest problems facing those working in the earth sciences is the accurate determination (5 - 10%) of trace element contents. Until very recently, emission spectrography was the chief tool of the geochemist in his attempts to measure traces of the elements in materials of geologic significance. However, conflicting results were often obtained and considerable question has arisen concerning the reliability which may be placed in optical spectrographic results. Of late, however, other methods of trace element analysis have been developed, chief among which is the method of isotope dilution. Isotope dilution appears to be easily the most promising method of investigation of traces of the elements as far as absolute accuracy is concerned. The major drawback to the method is that it requires a mass spectrometer, an instrument for which the initial outlay of money is high and which requires expensive maintenance and trained operators. Another, less serious, disadvantage is the fact that the method requires much time, not only in the processing and analysis of the samples, but also for computation and evaluation of the data recorded. However, these disadvantages are completely overshadowed by the major advance of accuracy.

Isotope idlution has come of age only within the past few years as the result of improvements in the design and operation of mass spectrometers and the availability of stable isotope tracers made possible by the Atomic Energy Commission. The method has been described by a number of investigators, e.g. Inghram (1954), Tilton (1954). Isotope dilution is a method of analysis in which the relative abundances of the naturally occurring isotopes of an element are altered by the analyst. This alteration of the relative abundances of the naturally occurring isotopes of an element are altered by the analyst. This alteration of the relative isotope abundances within the analysis element is accomplished through the addition of a known amount of stable isotope tracer, obtainable from the A.E.C. The stable isotope tracer, generally referred to as "spike", is a sample of the analysis element in which the relative abundances of the isotopes present have been artificially altered. The relative abundances of the isotopes of the spike must, of course, be determined mass spectrometrically before the spike can be used for isotope dilution analysis.

The method followed by the A.E.C. in the preparation of a spike is to run a sample of the element in a large mass spectrometer; the material, collected at the collector and has been partially separated isotopically, and, if recovered, will have relative isotopic abundances different from those in the normal element. Theoretically, each isotope of an element could be collected. In actual practice, however, this would require a great deal of time and expense in order to obtain samples large enough to be of use to the analyst.

The spike obtained from the A.E.C. is made up into a solution of known concentration. A known amount of this solution is then added to a known amount of the material to be analysed. The whole, sample and spike, is then taken into solution resulting in a homogeneous mixture of spike and the analysis element. As a result of this mixing of spike and normal element, the relative isotopic abundances when measured on the mass spectrometer will be found to lie somewhere between those in the pure spike and in the pure, unaltered element. Then, if we know:

(a) the relative abundances of the isotopes in the pure spike
(b) the relative abundances of the isotopes in the normal element
(c) the weight of the spike added
(d) the weight of the sample in which the concentration of the analysis element is to be determined
(e) the ratio of any two non-radiogenic isotopes of the analysis element resulting from the mixture of spike and normal element,

the ratio of the weight of normal element to spike element present in the mixture may be calculated and the concentration of the element can be found.

The great advantage to isotope dilution analysis is the fact that a perfect internal standard is used. In other methods of analysis this is not the case. For example, in emission spectrography, it is extremely difficult to find an internal standard element that will follow perfectly the analysis element. Indeed, it has been found that although two elements may follow one another perfectly in one type of material, they may not in another due to differences in the matrices of the materials being analysed. This problem has also been recognized in X-ray fluorescence and flame photometric analysis. In the isotope dilution method, on the other hand, the internal standard element and the analysis element are one and the same thing, the only difference being in their isotopic compositions. They should thus react in the same way to physical and chemical influences. Figure I illustrates the isotopic abundances in the rubidium spike used in this research, the isotopic abundances in normal rubidium, and the isotopic abundances which would result from a mixture of equal amounts of each.

Isotopic abundances in the spikes. In order to determine the relative abundances of the isotopes in the spikes used in this research, a number of pure spike samples have been analysed mass spectrometrically. Table IX shows the results of isotopic analyses carried out on pure strontium spike.

TABLE IX

Run No.	Date	No. of sets	84	86	87	88
1	2/16/54	270	.4605	.1445	.0887	.3063
2	3/7/55	30	.4595	.1442	.0892	.3071
3	5/1/56	540	.4608	.1434	.0877	.3081
Weighted average:			.4607	.1438	.0881	.3075
A.E.C. value:			.4595	.1439	.0880	.3086

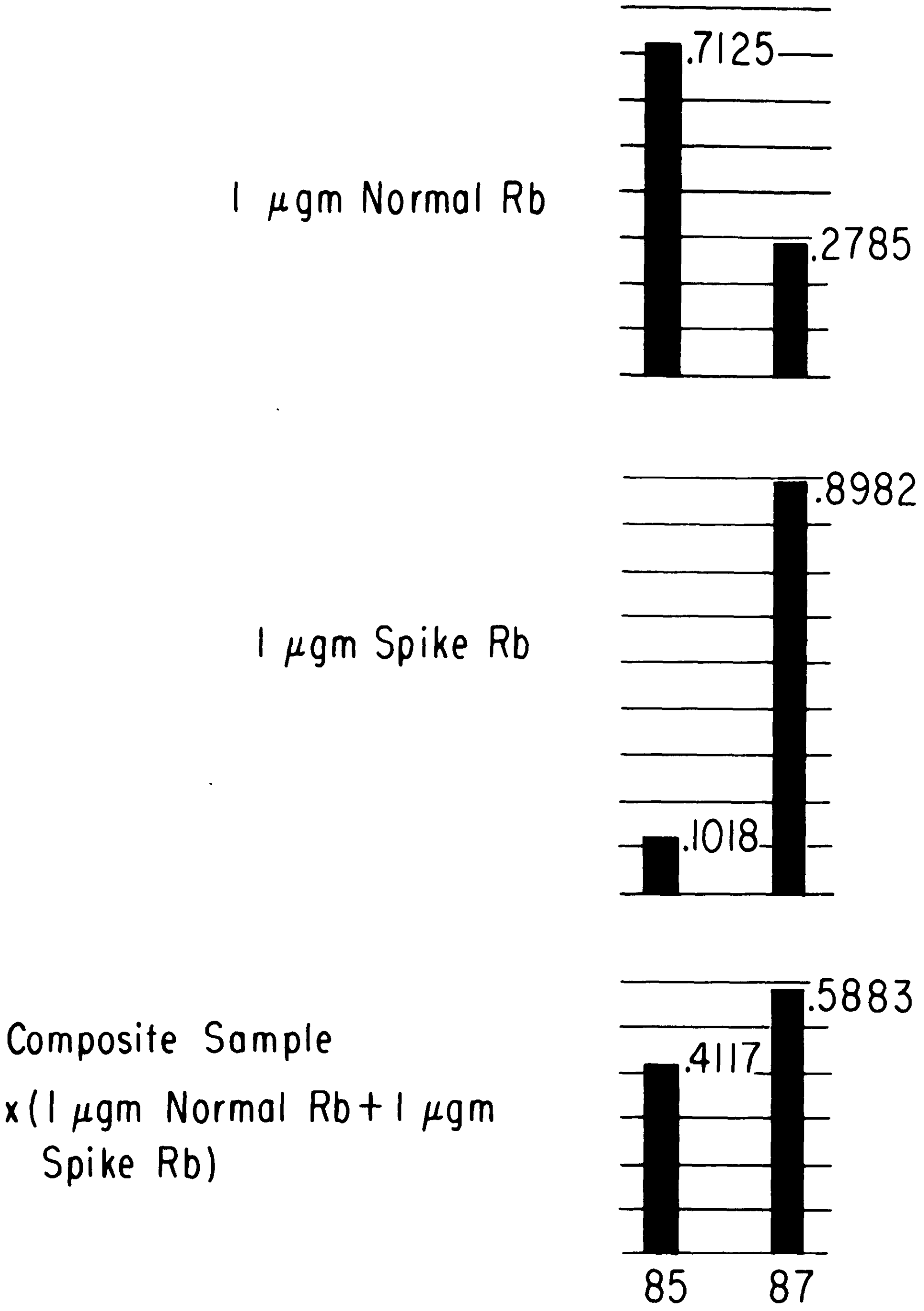
1 μgm Normal Rb
.7125
.2785
1 μgm Spike Rb
.8982
.1018
Composite Sample
x(1 μgm Normal Rb + 1 μgm Spike Rb)
.5883
.4117
85
87

Fig.I

The agreement among the abundances of Table II is good. The abundance of the Sr^{87} isotope shows the greatest spread (1.7%). It is of the utmost importance to know accurately the abundance of Sr^{87} in the spike, since it is used to calculate the concentration of radiogenic strontium in samples analysed for age determination work. Small changes in this abundance can cause changes in the apparent age of a sample, the magnitude of these changes increasing rapidly as the concentration of the radiogenic strontium and the age of the sample decrease. It was found, for example, that in determining the age of an Upper Cretaceous glauconite, merely changing the Sr^{87} abundance in the spike from .0890 to .0885 resulted in a 100% or larger change in the apparent age. It soon became obvious that to increase the accuracy of Rb/Sr glauconite ages, a method would have to be found in which the Sr^{87} abundance of the spike would not be critical. This was done, and the method used is described in Chapter V.

A review of the data gathered in the three runs carried out on the strontium spike at M.I.T. shows that in Run No. 1 rubidium contamination was present for at least half the run. Since rubidium has an isotope of mass 87, any rubidium present during a strontium run tends to enhance the height of the 87 peak. The other isotope of rubidium, at mass 85, is not interfered with by strontium since, fortunately, strontium has no isotope of mass 85. If the ratio of 85/87 is known for the contaminating rubidium, then a correction may be made for any contribution made by rubidium 87 to the strontium 87 peak. The normal ratio of Rb^{85}/Rb^{87} was used to correct for rubidium in Run No. 1. However, it has been learned, since this run was made, that in some instances the contaminating rubidium present during strontium analysis does not possess a normal ratio Rb^{85}/Rb^{87}. Its isotopic composition has been changed as a result of mixing with spike rubidium. This is probably due to "memory effects" within the mass spectrometer from previous rubidium isotope dilution analyses. When this occurs, it is obvious that no correction for rubidium contamination of strontium can be made. If such non-normal rubidium contamination were present in Run No. 1, the correction applied to the 87 peak for rubidium 87 contamination would be too small, since contamination of normal rubidium with spike rubidium lowers the ratio of Rb^{85}/Rb^{87}. This in turn would lead to a Sr^{87} abundance that was too high.

Run No. 2 is actually of little consequence, since only a very small amount of Sr emission was obtained and the run might even be considered unsatisfactory. Its effect on the weighted average, however, is small because of the small number of sets collected during the run.

Run No. 3 was an excellent run. Copious strontium emission was obtained, there was no rubidium contamination whatsoever, a great many sets of data were collected, and the sample was run to completion.

Table X is a tabulation of the results obtained from the isotopic analysis of the pure rubidium spike which was used in this research.

TABLE X

Run No.	Date	Sets	85	87
1	12/15/54	125	.1018	.8982
2	8/16/56	178	.1030	.8870
Weighted average:			.1024	.8976
A.E.C value:			.1038	.8962

It will be noted that in Table X the abundances obtained in Run No. 1 differ significantly from those obtained by the A.E.C. and to a lesser extent, with these obtained in Run No. 2. It seems possible that this may be due to contamination of the A.E.C.s sample by normal rubidium and the same may be true, though to a lesser extent, in the case of Run No. 2. Such contamination of the spike would increase the abundance of the 85 isotope and decrease the 87 isotope abundance. Contamination at M.I.T. could only be with normal rubidium, and because of this, the value obtained in Run No. 1 may represent a maximum value for the Rb^{85} abundance in the spike. However, this is not known with certainty and, for the work reported here, the weighted average of runs 1 and 2 have been used.

Isotopic abundances in normal strontium. Table XI lists the values obtained by various analysts for the relative abundances of the isotopes of strontium. The writer has carried out and assisted in a number of isotope analyses of strontium samples extracted from various geologic materials in which the ratio Sr/Rb was high. Results of these analyses are shown in Table

XII. These analyses were carried out with the objective of determining the relative isotope abundances in common or normal strontium. Strontium in general is either "common" or for lack of a better name, "uncommon". Common strontium is that which has existed in an environment in which the ratio Sr/Rb is high (~5/1). The strontium contained in the oceans, in limestones, and in the plagioclase feldspars is of the common variety.

TABLE XI

Investigator	84	86	87	88
Sampson and Bleakney (1936)	.005	.096	.075	.824
Nier (1938)	.0056	.0986	.0702	.8256
White and Cameron (1948)	.0055	.0975	.0696	.8274
Aldrich and Herzog (1952)	.0058	.0987	.0703	.8252

TABLE XII

Sample	Run No.	84	86	87	88
Grenville celestite	1	.0056	.0987	.0701	.8256
Grenville celestite	2	.0055	.0982	.0699	.8264
Grenville celestite	3	.0054	.0981	.0696	.8269
U.S. Bur. Stds. $SrCO_3$	1	.0056	.0985	.0703	.8256
U.S. Bur. Stds. $SrCO_3$	2	.0056	.0987	.0703	.8254
Sea water	1	.0056	.0986	.0700	.8258
Iswos limestone	1	.0056	.0984	.0702	.8258
Averages:		.0056	.0985	.0701	.8258

The second type of strontium, uncommon strontium, is that which has existed in an environment in which the ratio Sr/Rb is very low. Strontium found in rubidium rich minerals such as lepidolite, biotite, muscovite, glauconite and potash feldspar is of the uncommon variety. The only real difference between the two types of strontium is that in the uncommon variety, the abundance of the 87 isotope is found to be significantly greater than in common strontium. This, of course, is due to the addition of radiogenic Sr^{87} from the high rubidium environment.

The strontium utilized for Rb/Sr age determinations is of the so-called uncommon variety, that is, it has been extracted from material possessing a high Rb/Sr ratio. In nearly all cases, a certain amount of strontium was included in these materials at the time of their formation. If this were not so, then we would expect the strontium extracted from such materials to be composed entirely of radiogenic Sr^{87}. Except in the case of some lepidolites, the strontium extracted from rubidium rich minerals is found to contain considerable amounts of the non-radiogenic strontium isotopes.

When measuring the Rb/Sr ages of minerals, then, the analyst must have a knowledge of the isotopic composition of the strontium originally included in the mineral at the time of its formation. The isotope abundances given in Tables XI and XII indicate that the isotopic composition of strontium extracted from materials possessing a high Sr/Rb ratio, that is, common strontium, is essentially contant. Since glauconite forms only in sea water, it would seem probable that the strontium included in glauconites at the time of their formation would possess an isotopic composition similar to that of strontium found in sea water, or in materials deposited from sea water such as limestone. The strontium of celestites is probably also representative of sea water strontium since the celestite generally occurs in limestone. Although the celestite may not be primary, its strontium probably was derived from the enclosing limestone. In the light of these considerations, it was felt that the isotopic composition of strontium included in glauconite at the time of its formation would follow very closely the values given in Table XII. These values represent those of strontium samples all thought to have originated from sea water. As a check on this conclusion, strontium samples were extracted from 15 glauconites and these were analysed isotopically. It was found that in all cases but one, the ratios Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} are very similar to those of the samples given in Table XII. Ratios involving Sr^{87}, of course, could not be compared because of the differences in Rb/Sr ratios of the materials compared. The results of glauconite strontium analyses are shown in Table XIII. Average values of the ratios Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} for Tables XII and XIII are seen to be almost identical. Although the major part of the variations noted are within the limits of error of the determinations, it seems almost certain that small variations in relative isotope abundances do occur.

Isotopic abundances in rubidium. The element rubidium is composed of two isotopes of mass 85 and 87. Values of the ratio Rb^{85}/Rb^{87}, as reported by various investigators, are shown in Table XIV.

TABLE XII

RESULTS OF ANALYSES OF Sr EXTRACTED FROM GLAUCONITE

Sample	Isotope Abundances				Isotope Ratios			
	84	86	87	88	84/88	86/88	87/88	87/86
Gl-2	.0055	.0982	.0729	.8234	.00675	.1192	.0885	.7424
Gl-8	.0055	.0973	.0859	.8113	.00680	.1200	.1059	.8818
Gl-10	.0054	.0968	.0743	.8235	.00659	.1176	.0902	.7673
Gl-11	.0056	.0966	.0951	.8027	.00696	.1203	.1185	.9850
Gl-12	.0054	.0953	.0983	.8010	.00680	.1190	.1227	1.0311
Gl-13	.0057	.0981	.0736	.8226	.00688	.1193	.0895	.7489
Gl-14	.0057	.0987	.0754	.8202	.00695	.1203	.0919	.7639
Gl-15	.0058	.0973	.0780	.8189	.00713	.1188	.0952	.8025
Gl-16	.0055	.0977	.0773	.8195	.00674	.1192	.0943	.7909
Gl-17	.0056	.0989	.0710	.8245	.00684	.1200	.0861	.7167
Gl-18	.0055	.0980	.0706	.8259	.00667	.1186	.0855	.7203
Gl-20	.0055	.0970	.0829	.8146	.00674	.1191	.1018	.8547
Gl-21	.0055	.0967	.0835	.8143	.00671	.1188	.1025	.8628
Gl-22	.0055	.0969	.0796	.8180	.00670	.1184	.0973	.8218
Normal Sr	.0056	.0985	.0701	.8259	.00678	.1193	.0849	.7117
Averages					.00680	.1193		

TABLE XIV

Investigator	Rb^{85}/Rb^{87}	
Brewer and Kerek (1934)	2.58	.02
Brewer (1938)	2.60	
Nier (1950)	2.591	.006
Herzog et al (1953)	2.591	.003

The value 2.591 has been adopted for the work reported on here. As is obvious from Table XIV, very little variation in the relative abundances of the rubidium isotopes has been found.

Fractionation of isotopes. Variations in the relative abundances of isotopes may be introduced as a result of fractionation of the isotopes in response to physical or chemical processes. Fractionation of strontium isotopes during their mass spectrometric analysis has been observed by a number of investigators. Fractionation apparently occurs during the evaporation of the sample from the filament. During the early portions of the run, the proportion of lighter isotopes in the emitted beam is abnormally high, while in the latter part of the run, the reverse is true. Fractionation of Sr isotopes during analysis is illustrated in Figure Ia. Backus (1955) reports a change of 17% in the ratio Ca^{40}/Ca^{48} during the mass spectrometric analysis of a calcium sample. The maximum fractionation of strontium isotopes noted in this laboratory was about 3% for the ratio Sr^{84}/Sr^{88}. Fractionation of rubidium isotopes during analysis has not been observed, but is probably present.

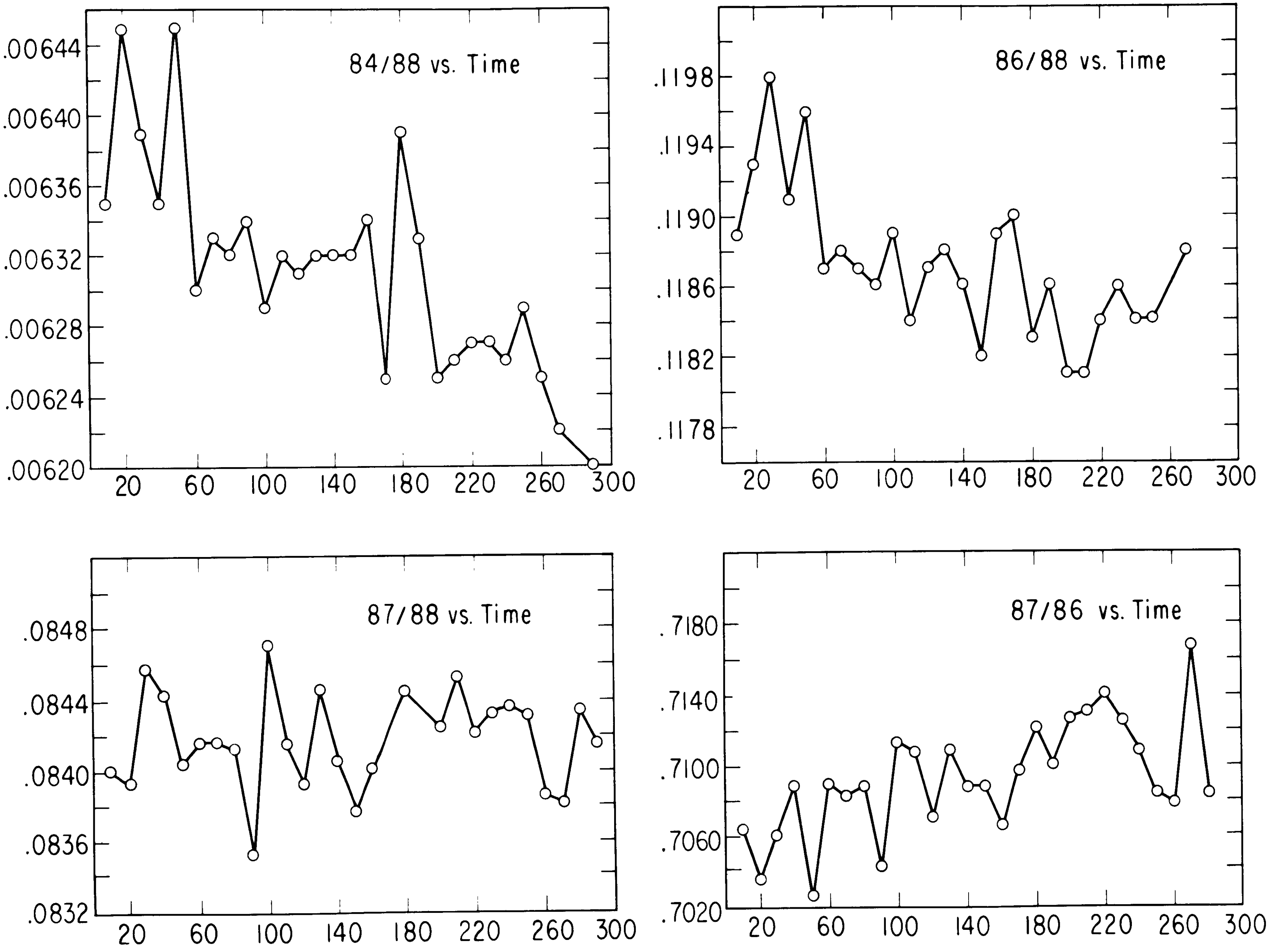

Fig.Ia

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It is not known whether or not the isotopes of strontium or rubidium fractionate as a result of processes operative in nature. Analyses of strontium extracted from glauconites (Table XIII) show some variations in the ratios Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} which could quite possibly be due to natural fractionation. Where natural fractionation of the isotopes is suspected, a correction must be made in order that the age calculated for the glauconite may be strictly comparable with those found for other glauconites. This follows from the fact that any such fractionation will result in a change in the abundance of Sr^{87} in the glauconite, which, in turn, will affect the radiogenic strontium calculation. In only one case out of the fifteen glauconite strontium samples analysed (Gl-10) was it found necessary to correct for what appeared to be significant natural fractionation.

In order to make a correction for fractionation, the relationship between degree of fractionation and the relative masses of the isotopes concerned must be known. It has generally been assumed that the degree of fractionation resulting from physical or chemical processes is proportional to

$$\sqrt{\frac{M_1}{M_2}} - 1 \qquad (1)$$

where M_1 is the heavier and M_2 the lighter of the two isotopes concerned. This relationship has been found to be applicable, within limits of error, to the cases of fractionation during analysis observed in this laboratory. Substituting in (1) the values for the strontium isotopes, we see that the degree of fractionation for the ratio Sr^{88}/Sr^{84} would be 0.0235 while that for the ratio Sr^{86}/Sr^{84} would be 0.0118. Thus, if fractionation occurred, the value of the ratio Sr^{88}/Sr^{84} would be affected twice as much as the value of the ratio Sr^{86}/Sr^{84}. It is also assumed in correcting for fractionation that the strontium which was present in the sea water at the time the glauconite formed had the same isotopic composition as the average values given in Table XII. Thus, if the ratio Sr^{88}/Sr^{84} was found to be 3% low in a strontium sample extracted from a glauconite, then the ratio Sr^{86}/Sr^{84} should be 1.5% low, and the ratio Sr^{87}/Sr^{84} in the original strontium incorporated in the glauconite at the time of its formation (which cannot be measured directly because of subsequent additions of radiogenic Sr^{87}) should be 2.25% lower than the value accepted for common strontium. On this basis, then, the original abundances of the strontium isotopes present in the glauconite after fractionation had occurred, but before radiogenic strontium had been added, were calculated.

Actually, however, as was stated above, only very minor variations were found in the non-radiogenic isotope ratios of strontium extracted from the glauconites and only in the case of Gl-10 was significant fractionation thought to have occurred.

Calibration of spike solution. It is of the utmost importance in isotope dilution analysis that the concentrations of the spike solutions used be known very accurately. The quantities of spike obtained from the A.E.C. are necessarily small, although large enough for their purpose. In making up a strontium or rubidium spike solution, one must weigh out a quantity of spike, the weight of which is of the order of 20-30 mg. When working with such small quantities, weighing errors could easily be large. The uncertainty thus introduced in the concentration of the spike solution necessitates calibration of the spike in some fashion. The method used for spike calibration in this work is to prepare a solution of normal strontium of known concentration by weighing out a large amount (1-2g.) of normal strontium, in this case Eimer and Amand Reagent $SrCO_3$, Lot No. 492327. Because of the large amount used, weighing errors are negligible. The weighing procedure is that recommended in standard texts on quantitative analysis. The procedure is as follows:

(1) Thoroughly clean two marked weighing bottles, dry at 110°C, and cool in a dessicator. Determine weight difference with an analytical balance.

(2) Repeat drying and weighing until three identical weight differences are obtained in succession.

(3) Add 1-2 g. $SrCO_3$, which has been thoroughly dried and cooled in a dessicator, to one of the bottles and de-

termine the resulting weight difference. Drying, cooling, and weighing are repeated until three identical values are obtained in succession.

The weight of $SrCO_3$ used is then known. This is taken into solution with dilute HCl in the weighing bottle and transferred quantitatively to a volumetric flask. The sample is then diluted to the desired concentration.

To a known volume of the spike solution to be calibrated is added a known volume of the standard strontium solution. The mixture is evaporated to dryness to insure complete mixing of the two. The strontium is then precipitated as the oxalate, placed in the mass spectrometer and analysed isotopically. The weight of spike strontium present in the known volume of spike solution used can then be found. In effect, we have performed an isotope dilution analysis in which standard or common strontium serves as spike. Table XV shows the results of strontium spike calibrations carried out in this laboratory.

The excellent agreement exhibited, not only between replicate calibrations, but also between the predicted (from weighing) values and analysed values, is apparent. Most of glauconites reported here were analysed using spike solution III, with spike solution IV being used for the last few analyses.

TABLE XV

Spike Solution	Date Run	$\frac{\text{Atoms Normal Sr}}{\text{Atoms Spike Sr}}$	Predicted	Measured
I	12/10/54	.9937	62.9μg/ml.	61.9μg/ml
II	2/16/55	2.9214	6.29	6.29
III	3/23/55	.9960	37.9	35.4
III	4/30/55	.4973	37.9	35.3
III	11/5/55	2.038	37.9	36.0
IV	6/29/56	1.1366	21.0	20.3
IV	7/3/56	.7672	21.0	21.0

Table XVI is a tabulation of the results obtained from calibration of rubidium spike solutions.

TABLE XVI

Spike Solution	Date Run	Atoms N/S	Predicted	Measured
I	12/22/54	.9240	87.3μg/ml	81.4μg/ml
I	2/14/55	.3359	87.3	80.5
II	5/1/55	.9887	54.9	54.1
II	11/3/55	.3341	54.9	54.2
II	7/1/56	1.3544	54.9	55.0
IA	10/31/55	.3307	1.62	1.61
IA	1/16/56	.2022	1.62	1.64

In the case of the glauconite analyses reported here, Spike Solution II was used throughout. A straight average of the three calibrations was used.

Probably the best manner in which to check the accuracy of the isotope dilution analyses of a given laboratory is to have another laboratory analyse the same samples independently, using their own spike solutions, calibrations, etc. This has been done in the case of a number of lepidolite samples prepared and distributed by this laboratory. These have been analysed by the M.I.T. group, the D.T.M. group, and by Schumacher at the Institute for Nuclear Studies at the University of Chicago. A paper comparing the results obtained by the laboratories is currently being prepared (Herzog, Pinson, Backus, and Hurley). It can be stated now that the agreement in the measured ages obtained by the three laboratories was excellent. This was true, even though in most cases the samples analysed were found to contain significantly different amounts of daughter and parent element. Such reproducibility of results between laboratories is the best indication we have that isotope dilution analyses are accurate to at least 3%.

CHAPTER IV

SAMPLE SELECTION AND PROCESSING

The objective of this research was the setting up of an absolute time scale for the Paleozoic and Mesozoic eras. Samples of glauconite were obtained from six periods in these eras, although large unfilled gaps in the time scale remain. It is hoped, however, that glauconites from the remaining periods will soon be analysed, and many geologists have already offered to collect glauconite specimens which should go a long way toward filling these gaps. The following is a brief description of the specimens upon which work was done in this research. Two numbers are given for each specimen, the first being that assigned by the writer, the second being the number assigned the specimen in P.M. Hurley's departmental catalogue of specimens at M.I.T.

Gl-1 (R3210) LODI SHALE; Upper Cambrian; Western Wisconsin; Loc. 146-Ser. 26, T.12N., R7W. Collected by R.R. Shrock. This specimen is in the M.I.T. sedimentology collection and is numbered S20-49. Specimen is well laminated, the bedding planes being characterized by abundant glauconite grading gradually into glauconite-free arenaceous-argillaceous material. Individual lamina are about 1/2" in thickness. Two separate glauconite samples, Gl-1(a) and Gl-1(b), were separated. Gl-2 (R-3211) Mount Whyte Formation; glauconitic sandstone; upper Lower Cambrian; Brazeau River, Rocky Mountains, Alberta, Canada; collected by M.D. Kostoker. Specimen was obtained from the M.I.T. sedimentology collection and was numbered S6-164. Composed of coarse grains of glauconite (2-3mm.) in a very fine grained calcareous arenaceous matrix. Two glauconite samples were separated, Gl-2(a) and Gl-2(b).

Gl-3(K-3212) Glauconitic limestone; Lowest Ordovician; Sten-
Gl-11)

brottet, Sweden, 10 Km. southeast of Falkoping, Vastergotland; Donated by H.B. Whittington, Harvard University. Specimen is composed of about 50% glauconite, rather coarse in grain (1-2mm.) in a matrix of crystalline calcite and what appear to be angular fragments of a very fine grain limestone. Pyrite is abundant. Two separate glauconite samples were taken from this specimen, Gl-3 and Gl-11.

Gl-4 (G-3213) Glauconite sand; Upper Cretaceous, New Jersey. Specimen is located in M.I.T. sedimentology collection and is numbered S13-7. It is in a short, rectangular bottle labelled "1858, Glauconitic Greensand, Cretaceous of N.J." The material is unconsolidated and is composed of about 90% glauconite. It is thought that this specimen may have been collected by William Barton Rogers.

Gl-5 (K-3215a) Glauconitic limestone; <u>Mount Whyte Formation</u>;
Gl-6 (K-3215b)

upper Lower Cambrian; Nigel Pass, Rocky Mountains, Alberta, Canada. Collected by M.D. Kostoker. This specimen was obtained from the M.I.T. sedimentology collection (S10-235). Specimen is a dark grey, fine grained limestone with small grains of glauconite peppered throughout. Two fractions of glauconite were separated, one (Gl-5) being lighter in color and less magnetic than the other (Gl-6).

Gl-7 (R-3216) Glauconitic limestone; Cambrian; Bridger Range, Montana. Specimen donated by VanHouten of Princeton University. This was a very small specimen composed of fine grained limestone pods of glauconite 2-3mm. in diameter scattered sparsely throughout. Only one sample of glauconite was separated from this specimen.

Gl-8 (R-3217) Glauconitic limestone; upper Lower Ordovician; Iswos, south shore of Lake Ladaga, Leningrad area, Russia. Collected by P.E. Raymond (1914); donated by H.B. Whittington, Harvard University. Specimen is a fine grained, well consolidated although somewhat earthy looking, limestone containing discrete grains of grass-green glauconite scattered throughout. Under the binocular microscope, many of the grains are seen to be casts of shelled animals. One glauconite sample was separated from this specimen.

Gl-10 (R-3214) Glauconite sand; Upper Cretaceous of New Jersey. This specimen is located in the M.I.T. sedimentology collection and is numbered S13-7. It was taken from a long, narrow, test-tube like, glass vial. Both Gl-4 and Gl-10 are in the same box in the collection and have the same number, but it is doubtful whether they were collected at the same time and at the same place. The material is unconsolidated and is at least 90% glauconite.

G1-12 (R-3219) Glauconitic sandstone; Franconia formation; Upper Cambrian; Readstown, Wisconsin. Collected by C.S. Baye. This specimen is in the M.I.T. sedimentology collection and is numbered S21-7. It is a finely laminated, quartzose sandstone with fine grains of glauconite peppered throughout. Two samples of glauconite, Gl-12(a) and G-12 (be) were separated.

G1-13 (G-3220) Glauconite; top 2 feet of Navesink Formation; Upper Cretaceous; Iversand County, Clayton, New Jersey. Donated by Dorothy Carroll, U.S.G.S. This sample is a glauconite which was separated and purified by Miss Carroll. Her number for the sample is DC-2.

G1-14 (G-3221) Glauconite; Hornerstown Formation; Lower Eocene; Iversand County, Clayton, New Jersey. This sample was taken immediately above Gl-13. It also was separated and purified by Miss Carroll. Her number for the sample is DC-3.

G1-15 (R-3222) Glauconitic sandstone; Lion Mountain Sandstone Member, Riley Formation; late-early Late Cambrian; Kendall County, Texas; U.S.G.S. Loc. 1988. Donated by A.R. Palmer, U.S.G.S. Specimen is a piece of core from Magnolia No. 1 -- below 6350 feet. Specimen is a very dark green in color and is composed of about 60% glauconite. Glauconite is intimately admixed with calcareous material. One glauconite sample was separated from this specimen.

Gl-16 (R3223) Glauconitic sandstone; Lion Mountain Sandstone Member, Riley Formation; late-early Late Cambrian; Little Llano section, Central Texas; U.S.G.S. No. LL-bb7. Collected and donated by A.R. Palmer, U.S.G.S. This specimen is thought to be the surface equivalent of Gl-15. Specimen consists of 30-40% glauconite in fine grained to coarsely crystalline calcite and arenaceous material. One sample of glauconite was separated from this specimen.

Gl-17 (R-3224) Glauconitic clayey siltstone; Redwater Shale Member of Sundance Formation: Upper Jurassic; Flattop anticline, west end, Laramie Basin, Wyoming. Collected by George N. Pipiringos, donated by Ralph Imlay, U.S.G.S. Specimen is a siltstone, dark brown in color and somewhat earthy looking. Glauconite is yellowish green and difficult to see in the hand specimen. One glauconite sample was separated from this specimen.

Gl-18 (R-3225) Glauconitic basal clay-siltstone; Redwater Shale Member of Sundance Formation; Upper Jurassic; Como anticline, west end, Laramie Basin, Wyoming. Collected by George N. Pipiringos, donated by Ralph Imlay, U.S.G.S. Specimen is identical in appearance to Gl-17. Glauconite is light green in color and occurs as tiny grains sprinkled throughout.

Gl-20 (R-3227) Glauconitic sandstone; Murray Shale of Chilhowee Group; Lower Cambrian; Blockhouse Quadrangle, Blount County, Tennessee. Donated by U.S.G.S. Specimen is a thinly laminated, somewhat iron stained, quartzose sandstone. Glauconite appears to be concentrated along bedding planes. "Lowest confirmed Cambrian fossils come from about 500' stratigraphically above this specimen."

Gl-21 (R-3228) Glauconitic limestone; Lower Ordovician; Wassilkowa, Leningrad area, Russia. Donated by H.B. Whittington, Harvard University. Specimen is a very fine grained, light colored limestone with scattered small grains of glauconite throughout. It is very similar in appearance to Gl-8 and comes from the same area. One glauconite sample was separated from this specimen.

Gl-22 (R-3268) Glauconitic siltstone; Carlisle Center Formation; Lower Devonian; quarry 1.3 miles NE of NY 145 and NY 7 in Cobleskill, N.Y. Collected by D.W. Fisher, New York State Paleontologist, 5/31/56. Specimen is a greenish-grey, calcareous argillaceous siltstone. Formation has produced no fossils save "Taonurus cauda-galli, which I (Fisher) believe to be a sea-weed but some believe to be worm markings." Carlisle Center overlain by Schoharie Formation or Onondaga Limestone in the absence of the Schoharie, underlain by Esopus shale.

Separation of glauconite. Glauconite bearing samples were crushed in a steel mortar which had been thoroughly cleaned with dilute HCl and water. The mortar was also pre-contaminated with a small portion of the sample to be crushed. After grinding, the sample was sieved. The size fractions found to be most suitable for glauconite separation were 100, 140, 200, and 270 mesh. After sieving, the samples were washed with acetone to remove dust-size particles clinging to the grains. It was found that this resulted in a much cleaner separation. The fractions were then passed through a Franz magnetic separator, as many times as was necessary, to obtain a clean split. In general the glauconite samples obtained were more than 95% pure. Rarely were they less than 90% pure. Heavy liquid separation was not used.

Chemical treatment of the glauconite samples. The sample was first weighed. All weighings were carried out on the analytical balance in the Cabot spectrographic laboratory at M.I.T., using calibrated weights. Generally, between two and three gram samples were taken. The sample was then transferred to a clean platinum crucible. It should be stated here that the term "clean" used in reference to laboratory utensils means that the vessel has been thoroughly scrubbed with a cleaning compound (Alconox), rinsed with tap water until all the cleaning compound has been removed, washed three times in 2N HCl, and finally washed three times with demineralized water. The HCl used in this research was distilled in a still of Vycor glass, which has low alkali and alkaline earth contents. All water used was M.I.T. distilled water that had been passed through an ion exchange resin demineralizer and was known to contain less than .01 ppm heavy metals expressed as NaCl. Isotope dilution analyses of this water disclosed the presence of 0.0003 ppm strontium and 0.0006 rubidium.

When the sample had been transferred to the platinum dish, it was wetted with a small quantity of water. Approximately 20cc of perchloric acid and 30cc of hydrofluoric acid were added, care being taken to avoid loss of sample through effervescence of carbonate which might be present in the sample (and often was). The sample was then taken almost to dryness over a low heat, great care being taken to avoid any spattering. An additional 15cc of hydrofluoric acid were then added in order to remove any traces of silicon. The sample was then taken to complete dryness and ignited gently to convert all perchlorates to chlorides and oxides. To the residue was added 30cc of HCl and this was taken to dryness to drive off any remaining hydrofluoric acid. If any were allowed to remain, leaching of alkalies from the glass might occur when the sample was placed in a glass container. The residue was taken into HCl solution and transferred quantitatively to a volumetric flask. Pouring the sample down a clean, glass rod was found to be the easiest and safest method of transferring it to the volumetric flask. The sample was allowed to cool to room temperature and was then diluted to exactly 100cc with 3N HCl.

As a general rule, in work of this nature, strontium and rubidium spikes are added before the sample is dissolved. This is good practice in that subsequent spattering during treatment of the sample will not introduce appreciable error, provided of course, that the strontium and rubidium in the glauconite do not have appreciably different solubilities. In this case however, it was desired to analyse unspiked strontium from the glauconite as well. Of course the glauconite sample could have initially been split into two fractions, one of which could be spiked at the very beginning while the other would be used for the separation of unspiked strontium. However, in order to make certain that the strontium analysed in the isotope dilution analysis and in the unspiked strontium analysis was the same, the sample was split for spiking after it had been taken into solution.

A 20cc portion of the sample is removed from the volumetric flask with a pipette and placed in a clean, Vycor glass evaporating dish. To this is added appropriate quantities of strontium and rubidium spike solution. The remainder of the sample is returned to the platinum dish and evaporated to a volume of approximately 20cc. It is then placed on an ion exchange column for separation of unspiked strontium for isotope abundance determination. The spiked portion of the sample is evaporated to dryness to insure complete mixing of the spike strontium and rubidium with the sample strontium and rubidium. The residue is taken into solution with about 10cc of 2N HCl and placed on another ion exchange column for separation of spiked strontium and rubidium for isotope dilution analysis.

<u>Separation of microgram quantities of strontium and rubidium.</u>* The ion exchange columns utilized in this research for the sep-

aration of strontium and rubidium were constructed using Dowex 50,8% cross-linked, 200-400 mesh cation exchange resin. The columns were constructed of Vycor glass tubing, one inch in diameter. The column resin was 12" in length and was composed of graded layers of resin about $\frac{1}{8}$" in thickness. The sample, in HCl solution, was placed on the column in as small a volume, and with as low a normality, as possible, without allowing it to come out of solution. This is necessary in order that a clean separation of the elements be attained. After the sample has soaked into the upper part of the column of resin, the walls of the column are washed down with 5-10cc of acid. When this also has soaked in, the column is filled with HCl which slowly passes down through the resin and drips out at the bottom.

The principle underlying ion exchange chemistry is the fact that the resin particles tend to adsorb the cations in the HCl solution. Cations of different elements are held with different strengths. The hydrogen ion is most strongly held and will gradually displace the other cations present on the surfaces of the resin particles. As a result of the different strengths with which the cations are absorbed, the various elements present in the solution travel the length of the column at different speeds. If separate fractions are collected at the base

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* Note: The techniques described here were developed largely by L.T. Aldrich and his group at the Department of Terrestrial Magnetism, Washington, D.C.

of the column, as acid is run through it, the elements present will be separated as a result of their different rates of passage through the resin. The order of appearance of the elements at the base of the column is: Fe, Li, Na, K, Rb, Cs, Ca and Sr. Figure II depicts the relative positions of the elements as a function of the volume of acid which has passed through the column. The rate at which the cations move through the resin is, of course, dependent upon the normality of the acid used. The higher the concentration of acid used, the more rapidly will the elements move through the column and the less will be the degree of separation of the elements. In the case of the Sr-Rb isotope dilution fraction,2N HCl is used until the potassium has come through the column. This ensures a fairly good separation of potassium and rubidium. After that, 3N acid is used since it has been found that acid of this normality gives a sufficiently clean strontium separation. 3N acid is used throughout for separation of the unspiked strontium sample.

Determination of just what fractions contain the strontium and rubidium is accomplished in the following manner: cavities are drilled in pure carbon electrodes and a few drops of each fraction are placed in an electrode. The fractions have been evaporated down to approximately one ml. in order to concentrate the elements present. The electrodes are dried under a heat lamp and are then arced on the Hilger spectrograph. The fractions found to contain the highest concentrations of strontium and rubidium are thus located and set aside for mass spectrometric analysis.

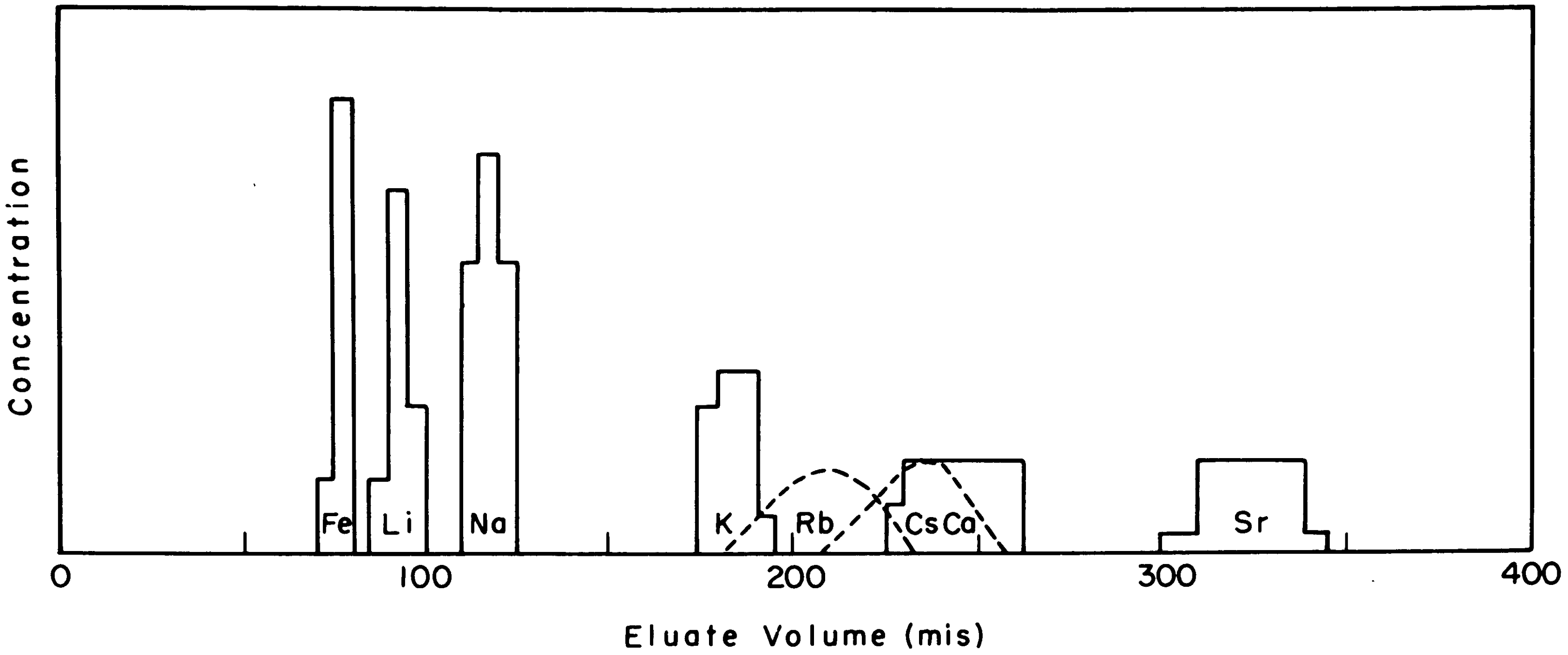


FIG. II - SEPARATION OF ALKALIS AND ALKALINE EARTHS BY ION EXCHANGE TECHNIQUES. THE APPLIED SAMPLE CONTAINED 0.06 GRAMS EACH OF Fe, Li, Na, K, Ca, AND Ba IN 3 mls. OF 3. ON HCl. THE COLUMN AND STANDARD TECHNIQUES USED ARE DESCRIBED IN THE TEXT

Preparation of samples for mass spectrometer.

A. Rubidium. The fraction found to contain the highest rubidium concentration is placed in a clean Vycor evaporating dish. A few drops of distilled nitric acid are added to it and the whole is evaporated to dryness. The residue, in which the rubidium is present as the nitrate, is dissolved in a drop or two of water, taken up in a clean pipette, and placed on the filament of the mass spectrometer source.

B. Strontium. The fractions containing the highest strontium contents are combined, placed in a clean Vycor evaporating dish, and evaporated to dryness. The residue is taken into solution with a few milliliters of water and a few drops of hydrochloric acid. A few grains of ammonium oxalate are dissolved in the sample and then an excess of distilled ammonium hydroxide is added. The sample is then evaporated almost to dryness. Care must be exercised not to allow the sample to go completely to dryness at this point or spattering and loss of sample will result. The sample dish is then placed in crushed dry-ice and allowed to cool. Ice water is added and the ammonium chloride present goes into solution. A fine, white, granular precipitate of strontium oxalate is left. Cooling of the dish and the use of ice water is necessary because at room temperature strontium oxalate is soluble to the extent of 0.005g per 100cc of water. The precipitate is then very carefully collected together in the bottom of the dish. The liquid present is pipetted off, using a polyethylene pipette. The precipitate is washed with ice water and the water pipetted off. Washing of the precipitate is repeated four or five times, if possible, in order to remove any traces of rubidium that might be present. Indeed, experience has shown that unless the precipitate has been washed at least twice, difficulty will be encountered as a result of rubidium contamination during the mass spectrometric analysis. After washing has been completed, the precipitate is drawn up into a pipette and is allowed to settle out on the filament of the mass spectrometer source.

Contamination during chemical processing of samples. In order to test the levels of rubidium and strontium contamination introduced as a result of chemical processing of the samples, blanks were run for both rubidium and strontium. This was done in the following manner: To a clean platinum crucible was added 20cc of perchloric acid and 30cc of hydrofluoric acid. Known volumes of strontium and rubidium spike solution were also added. The solution was evaporated to dryness and an additional 15cc of hydrofluoric acid were added and taken to dryness. Then, 150cc of hydrochloric acid were added to the dish and evaporated to dryness. An additional 100cc of hydrochloric acid was then placed in the dish and evaporated to about 5cc. This was placed on an ion exchange column, and the strontium and rubidium were separated and their fractions were located. They were prepared and placed on the filament in exactly the same fashion as described in the foregoing section. They were each analysed isotopically, and the amount of contamination introduced for each element was calculated. The blanks were thus subjected to exactly the same treatment given an ordinary sample.

Analysis disclosed the presence of 0.2μg of rubidium contamination. Since the average glauconite sample, subjected to the same treatment, contained about 700μg rubidium, rubidium contamination was seen to be negligible. Strontium contamination amounted to about 0.3μg. Since the average glauconite sample subjected to this treatment contained at least 20μg of strontium, and sometimes two or three times this amount, the error due to strontium contamination was certainly no greater than about 2%.

Contamination within the mass spectrometer. During the earlier phases of the work reported on here, ages obtained for a number of glauconites appeared to conflict seriously with geological evidence. In order to ascertain whether or not the conflicting results were due to analytical errors, replicate analyses of the same sample were carried out. The results indicated that, although strontium analyses were reproducible, rubidium analyses were not and showed large variations from run to run. The errors were not thought to be due to mistakes in the actual processing of the samples, that is, in spiking, weighing, etc.. It was concluded that the most probable source of rubidium contamination was within the mass spectrometer itself. Table XVII shows the results of replicate rubidium analyses that led to the conclusion that rubidium contamination was being introduced.

TABLE XVII

Sample	Run	Rb(ppm)
G1-3	Rb I.D.1.	295
	Rb I.D.2	186
	Rb I.D.3	220
G1-11	Rb I.D.1	260
	Rb I.D.2	278
G1-12	Rb I.D.1	130
	Rb I.D.2	207

At the time the analyses shown in Table XVII were made, rubidium was not being separated on the ion exchange columns before analysis. Rather, a few drops of the solution in which the glauconite had been dissolved were placed directly on the filament. A very approximate calculation showed that only about 0.05μg of rubidium were being placed on the filament in this manner. It seemed entirely possible that memory effects within the mass spectrometer could give rise to significant contamination when such small amounts of sample were employed. It was felt that the best, and possibly the only way, to deal with such contamination would be to overwhelm it completely by placing a much larger sample on the filament. Thus, in order to increase the amount of rubidium placed on the filament, it was decided to separate the rubidium from the remainder of the glauconite on the ion exchange columns before placing it on the filament. The amount of rubidium placed on the filament was thereby increased by a factor of at least 1000. Results of replicate rubidium analyses in which the rubidium was concentrated using ion exchange columns are shown in Table XVIII.

TABLE XVIII

Sample	Run	Rb(ppm)
Gl-3	Rb I.D.1	311
	Rb I.D.2	308
	Rb I.D.3	307
Gl-15	Rb I.D.1	233
	Rb I.D.2	227
	Rb I.D.3	230

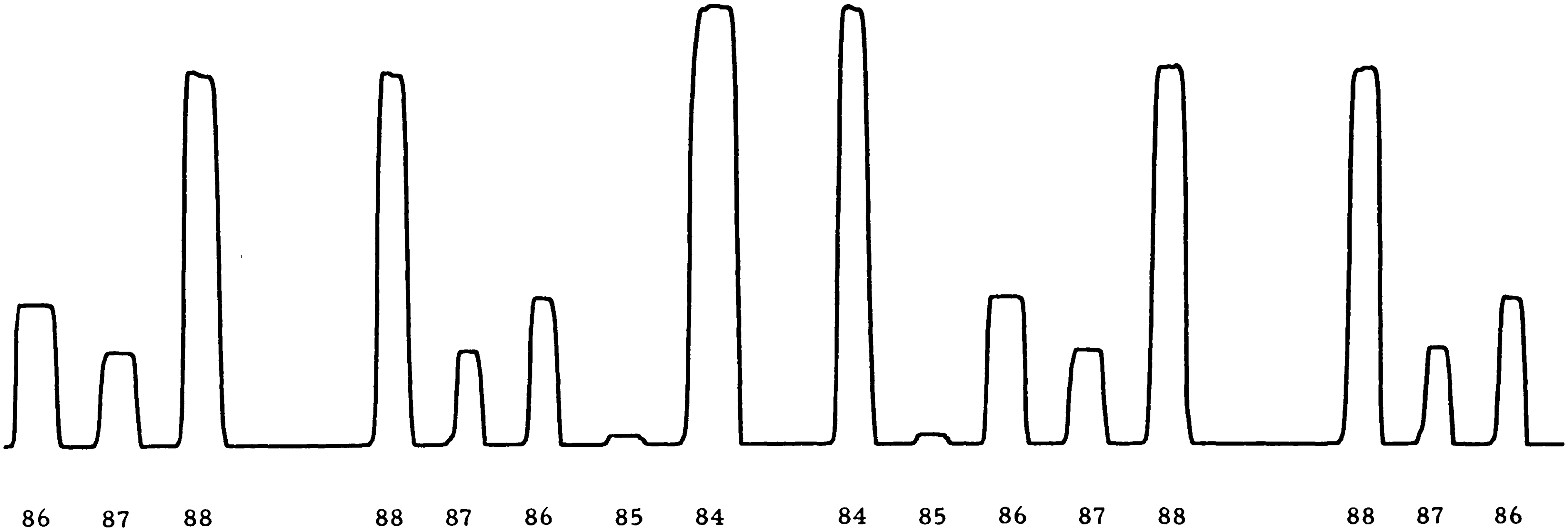
The excellent agreement between the replicate analyses of Table XVIII indicates that concentration of rubidium before analysis can overcome any contamination introduced within the mass spectrometer. Since that time, all rubidium samples analysed in this laboratory have been separated on ion exchange columns. All rubidium values reported in this work were obtained using samples enriched through ion techniques. Unfortunately, a number of glauconites analysed before the contamination problem was recognized could not be reanalysed due to insufficient quantities of sample.

CHAPTER V

TREATMENT OF THE DATA

Averaging of sets collected. There are two general methods employed in the collection of mass spectrometric data. The first is known as double collection and is a null method. The ion currents representing two masses are balanced, one against the other, by means of variable resistors. The ratio of the two masses involved may be read directly from the values of the resistances used to obtain balance. The second method employed is known as single collection. In this case the sizes of the various ion currents involved are measured using a recording potentiometer. A Weston or Brown strip chart recorder was used in our case. Only one ion beam falls into the collector at any given time and the peaks are recorded in succession on the chart. Both methods of collection have been utilized in this laboratory but the second method, single collection, was found to yield more accurate results. The data reported on here have all been gathered using single collection. An example of the data collected is shown in Figure III.

Since small but significant random variations occur in the ion currents, it is necessary to collect a rather large number of sets of data in any given run in order that the standard deviations of the ratios measured be acceptable. A set refers to a single sweep across the mass range of the element being measured. Thus, a rubidium set would be composed of two peaks



FigureIII Typical section of Weston Recorder record (unretouched) taken during analysis of ^{84}Sr-enriched tracer used in a chemical contamination experiment.

representing the two isotopes of rubidium at masses 85 and 87, whereas a strontium set would be composed of four peaks representing the four isotopes of strontium at masses 84,86,87, and 88. For rubidium analyses, approximately 80-100 sets were collected, while for strontium analyses, from 125-175 sets were taken. It should also be remembered that variations which are not random may be present during the course of a run, principally fractionation of the isotopes as they leave the filament. If fractionation is present, and if it is not reproducible from one run to another, it is necessary to run samples to completion in order that the fractionation not introduce significant errors in the ratios obtained from the run. Since fractionation of strontium isotopes as they leave the filament has been observed on numerous occasions in this laboratory (Herzog et al, 1954) and since the fractionation has not been found to be reproducible, the strontium analyses reported here represent runs in which the sample placed on the filament was run to exhaustion.

The sets collected were measured using a 60-scale engineering ruler. In the case of rubidium, the ratio Rb^{85}/Rb^{87} was computed for each pair of sets collected. For strontium runs, the ratios Sr^{84}/Sr^{88}, Sr^{86}/Sr^{88}, Sr^{87}/Sr^{88} were computed. It is necessary to compute the isotopic ratios from averages of pairs of sets rather than from single sets because of the fact that in most cases, the ion currents being recorded are either rising or falling to a certain extent, and only very rarely do they remain constant. After each pair of sets had been measured, averaged, and the ratios computed, the average of each ratio over the entire run was found. The standard deviation of the mean for each overall ratio was computed using the relation:

$$\text{Standard deviation of the mean} = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}}$$

where: $\bar{x}$ is the mean value of the ratio in question over the entire run.

x is the value of an individual ratio calculated from a single pair of sets.

n is the number of individual ratios computed over the entire run.

Calculation of rubidium and strontium concentrations. Rubidium and strontium contents are calculated from their respective isotope dilution runs in exactly the same fashion. To illustrate the method of calculation employed, an actual calculation of the strontium content of a glauconite will be given. It should be remembered that the strontium analyses in the isotope dilution run is composed of both normal strontium which was present in the glauconite and spike strontium which was added to it. We shall use the measured Sr^{84}/Sr^{88} ratio for the calculation.

Let: N equal the number of atoms of normal strontium present.

S equal the number of atoms of spike strontium present.

0.0056 equal the abundance of Sr^{84} in normal strontium.

0.4607 equal the abundance of Sr^{84} in spike strontium.

0.8256 equal the abundance of Sr^{88} in normal strontium.

0.3075 equal the abundance of Sr^{88} in spike strontium.

Then, the total number of Sr^{84} atoms in the sample is equal to $(0.0056N + 0.4607S)$ and total number of Sr^{88} atoms in the sample is equal to $(0.8256N + 0.3075S)$.

Therefore, $$Sr^{84}/Sr^{88} = \frac{(0.0056N + 0.4670S)}{(0.8256N + 0.3075S)}.$$

But, the ratio Sr^{84}/Sr^{88} has been measured mass spectrometrically to be 0.5835.

Therefore, $$0.5835 \doteq \frac{.0056N + .4607S}{.8256N + .3075S},$$

Cross multiplying and collecting terms,

$$0.4761N \doteq 0.2813S,$$

and $$N/S = 0.5908$$

The ratio of the number of normal strontium atoms to the number of spike strontium atoms is thus known. However, it is desired to find the ratio of the <u>weight</u> of normal strontium to the <u>weight</u> of spike strontium. The atomic weight of normal strontium is equal to 87.7091, while the atomic weight of spike strontium is equal to 85.7875, the differences of course being due to differences in their isotopic compositions.

Then, $$\frac{\text{weight of normal Sr}}{\text{weight of spike Sr}} = N_w/S_w = .5908 \times \frac{87.7091}{85.7875} = 0.6040$$

Now, the weight of spike strontium added to the sample was 35.6 μg.

Therefore, $$N_w = 35.6 \times 0.6040 = 21.5\,\mu g.$$

The 35.6 μg sample of spike strontium was added to 0.5270g of glauconite. Therefore, the concentration of normal strontium in the glauconite is:

$$\frac{21.5}{0.5270} = 40.8\mu g/g = 40.8ppm.$$

The calculation of the rubidium content of the glauconite parallels the above exactly. The value calculated for the rubidium content of this glauconite (Gl-15) was 230ppm.

<u>Calculation of radiogenic Sr^{87}.</u>

A. <u>From the isotope dilution run.</u> The strontium atoms of mass 87 in the sample analysed during the isotope dilution run are contributed by the spike strontium, the normal strontium included in the glauconite at the time of its formation, and the radiogenic strontium formed within the glauconite since the time of its formation.

Then, if: N equals the number of atoms of normal strontium present,

S equals the number of atoms of spike strontium present,

R equals the number of atoms of radiogenic strontium present,

0.0879 equals the abundance of Sr^{87} in the spike,

0.0702 equals the abundance of Sr^{87} in normal strontium,

0.8256 equals the abundance of Sr^{88} in normal strontium,

0.3075 equals the abundance of Sr^{88} in spike strontium,

$$Sr^{87}/Sr^{88} = 0.1690(\text{measured}) = \frac{0.0702N + 0.0879S + R}{0.8256N + 0.3075S} .$$

Cross multiplying and collecting terms;

$$0.0693N = 0.0358S + R.$$

But, $N/S = 0.5908.$

Substituting for N in terms of S,

$$(.0693 \times .5908)S - 0.358S = R$$

and, $R/S = 0.0051.$

Thus, the ratio of the number of radiogenic strontium atoms to the number of spike strontium atoms has been determined. In order to convert to the weight ratio, it is necessary to multiply by the ratio of the atomic weight of radiogenic strontium to the atomic weight of spike strontium. This ratio is equal to

$$\frac{87.0000}{85.7875} = 1.014.$$

Therefore: $R_w/S_w = 0.0051 \times 1.014 = 0.0052.$

Since the weight of spike strontium added was 35.6 μg, and the weight of the glauconite sample was 0.5270g, the concentration of radiogenic strontium is equal to:

$$\frac{35.6 \times 0.0052}{0.5270} = 0.35\text{ppm}$$

B. <u>From unspiked strontium isotope abundance run.</u> As was stated earlier, strontium extracted from most of the glauconites reported on here, to which no spike strontium had been added, was analysed isotopically. A second, more accurate, calculation of radiogenic strontium content can be made using this data provided only that the concentration of normal strontium in the glauconite is known from an isotope dilution analysis of the same sample. In order to illustrate, a calculation of radiogenic strontium content will be made using the concentration of normal strontium found in the isotope dilution analysis of the glauconite (Gl-15) and the data gathered in the isotopic analysis of an unspiked sample of the strontium contained in the glauconite.

It was shown that the normal strontium content of this glauconite was 40.8ppm. Isotopic analysis of strontium extracted from this glauconite showed the ratio Sr^{87}/Sr^{86} to be 0.8025. The strontium contained in this glauconite can be thought of as being composed of

(a) Common or normal strontium included in the mineral at the time of its formation, and

(b) Radiogenic Sr^{87} added to the mineral since its formation as a result of the decay of Rb^{87} contained in the glauconite.

The ratio Sr^{87}/Sr^{86} can then be broken into two parts, one part representing the ratio of normal Sr^{87} to Sr^{86}, the other part representing the ratio of radiogenic Sr^{87} to Sr^{86}. The ratio Sr^{87}/Sr^{86} in normal strontium was seen to be 0.7120. The ratio of radiogenic Sr^{87} to Sr^{86} in this sample will then be equal to (0.8025 - 0.7120), which is equal to 0.0905. This may be expressed in the following manner:

$$\frac{87^{c} + 87^{r}}{86} = \frac{87^{c}}{86} + \frac{87^{r}}{86} \quad ------ (1)$$

where the superscripts c and r refer to common and radiogenic respectively.

But, $\frac{87^c + 87^r}{86}$ was found to be equal to 0.8025 by mass spectrometric analysis, and $\frac{87^c}{86}$ is known to be equal to 0.7120.

$$\text{Therefore;}\quad \frac{87^r}{86} = 0.8025 - 0.7120 = 0.0905 \text{ - - - - - - } (2)$$

The ratios given in the above calculations are all ratios of numbers of atoms. Since we wish to find the weight of radiogenic strontium present, the values of the ratios given above must be converted to weight ratios by multiplying them by the ratio of the atomic weight of Sr^{87} to the atomic weight of Sr^{86}. The value of this number is 1.0116, and

$$(87^r/86)_w \quad 0.8118 - 0.7203 = 0.0915 \text{ - - - - - - } (3)$$

Now, since the concentration of common strontium present in the glauconite is known, from isotope dilution analysis, and since the weight abundance of Sr^{86} in common strontium is known, 0.0967, the concentration of Sr^{86} in the glauconite may be calculated. Thus,

$$\text{Concentration } Sr^{86} = 40.8 \times 0.0967 = 3.945 \text{ ppm ---} (4)$$

Substituting in (3)

$$\frac{87^r}{3.945} = 0.0915 \text{ - } (5)$$

$$\text{and, Concentration of } 87^r = .0915 \times 3.945 = 0.36\text{ppm - - - - } (6)$$

The radiogenic strontium concentration as calculated from the unspiked strontium analysis should be appreciably more accurate than that calculated from the isotope dilution run alone. There are two reasons for this:

(a) The concentration of radiogenic strontium calculated from the isotope dilution analysis alone is extremely sensitive to the abundance of Sr^{87} assumed to be in the spike. Very small changes (0.5%) in this abundance give rise to large variations in the concentration of radiogenic strontium calculated. The magnitude of such variations increases rapidly as the content of radiogenic strontium in the glauconite decreases. The calculation of radiogenic strontium content from the results of the unspiked strontium analysis is, however, independent of the abundance of Sr^{87} in the spike.

(b) The radiogenic Sr^{87} forms a greater proportion of the total strontium in the unspiked strontium run than it does in the isotope dilution strontium run. The error in the radiogenic strontium run then should be less when calculated from the unspiked strontium data. It can be shown, for example, that in the case of the glauconite just treated (Gl-15), the percentage of the total strontium in the isotope dilution run which was radiogenic was 0.32% while in the unspiked strontium run, radiogenic Sr^{87} formed 0.85% of the total strontium. Effectively, there was almost three times as much radiogenic strontium in the latter as in the former, so that the error involved should be cut by a factor of about three.

<u>Calculation of the age.</u> The general equation for the decay of a radioactive nuclide is:

$$N = N_o e^{-\lambda t} \qquad (1)$$

where, N_o is the number of atoms of the radioactive nuclide originally present,

N is the number of atoms of the radioactive nuclide left after a time t, and

λ is the decay constant.

The decay constant used in the work reported on here is $1.39 \times 10^{-11} yr.^{-1}$. This is the fraction of Rb^{87} which decays to Sr^{87} each year. This decay constant corresponds to a half-life for the Rb^{87} decay of 50×10^9 years. Returning to (1) above, since radiogenic Sr^{87} and Rb^{87} have the same mass, it can be shown that

$$N_o = N + R \qquad (2)$$

where R is the weight or concentration of radiogenic Sr^{87}, and N_o and N are the weights or concentrations of Rb^{87} originally present and present after time t respectively. Substituting in (1),

$$N = (N + R)e^{-\lambda t} \qquad (3)$$

$$\text{and } \frac{N}{N + R} = e^{-\lambda t} \qquad (4)$$

$$\text{then, } 1 + N/R = 1/e^{\lambda t} \qquad (5)$$

$$\text{and } e^{\lambda t} = 1 + R/N \qquad (6)$$

$$\text{and } \lambda t = \ln(1 + R/N)$$

$$\text{and } t = (1/\lambda)\ln(1 + R/N) \qquad (7)$$

Thus, if the concentration of radiogenic Sr^{87}, the concentration of Rb^{87}, and decay constant are known, the age of the mineral may be calculated. In the case of the glauconite used to illustrate, R was equal to 0.36 ppm., total rubidium was 230 ppm., and the decay constant was 1.39×10^{-11}. Since total rubidium was 230 ppm. and since Rb^{87} makes up 28.32% of total rubidium (by weight), the concentration of Rb^{87} present in the glauconite was (230 x .2832) which is equal to 65.0 ppm. Then,

$$t = 1/1.39 \times 10^{-11} \ \mathrm{ln.}(1 + 0.36/65.0) = 395 \times 10^{6} \text{ years.}$$

Calculation of standard errors.

A. **Calculation of error in normal strontium.** The standard deviation of the mean for the Sr^{84}/Sr^{88} ratio was found to be ± 0.25%. The standard deviations of the normal strontium and spike strontium isotope abundances are thought to be ± 0.25% also. Then,

$$Sr^{84}/Sr^{88} = 0.5835(\pm 0.25\%) = \frac{0.0056N(\pm 0.25\%) + 0.4607S(\pm 0.25\%)}{0.8256N(\pm 0.25\%) + 0.3075S(\pm 0.25\%)}$$

Cross multiplying, $0.4817N + 0.1794S = 0.0056N + 0.4607S$

$$\text{Error in } 0.4817 = 0.4817\sqrt{(0.0025)^2 + (0.0025)^2}$$
$$= 0.0017$$

$$\text{Error in } 0.1794 = 0.1794\sqrt{(0.0025)^2 + (0.0025)^2}$$
$$= 0.0006$$

Then, $0.4817N(\pm 0.0017) + 0.1794S(\pm 0.0006) = 0.0056N(\pm 0.0001) + 0.4607S(\pm 0.0012)$

Collecting terms and adding errors,

$$0.4761N(\pm 0.0018) = 0.2813S(\pm 0.0018)$$
$$N/S = 0.5908$$

$$\text{Error in } N/S = 0.5908\sqrt{\frac{(0.0018)^2 + (0.0018)^2}{(0.4761)^2 + (0.2813)^2}}$$
$$= 0.0044$$

Thus $N/S = 0.5908(\pm 0.044)$

Converting to weight ratio, N_w/S_w,$=0.5908(\pm 0.0044) \times 1.0223 = 0.6040(\pm 0.0045)$

The error in the weight of spike added is thought to be ± 2.0%.

The weight of spike added was therefore 35.6(±0.7)μg.

$$N_w = 35.6 \times 0.6040 = 21.5\mu g.$$

$$\text{Error in } N_w = 21.5\sqrt{\frac{(0.7)^2}{(35.6)^2} + \frac{(0.0045)^2}{(0.6040)^2}}$$

$$= 0.45$$

The weight of sample used was 0.5270g. and the error in this is insignificant in comparison to the error in the weight of spike added.

Thus, concentration of normal strontium is:

$$\frac{21.5}{0.5270} = 40.8\text{ppm.}$$

and the error in this concentration is:

$$\frac{0.45}{0.5270} = 0.9$$

Therefore, concentration of normal strontium in this glauconite is 40.8(±0.9)ppm.

B. Error in rubidium content. This calculation is carried out in exactly the same fashion as for the error in the normal strontium content. The error calculated for the total rubidium content was 230(±4.6)ppm., while the Rb^{87} content would thus be 65.0(±1.3)ppm.

C. Error in radiogenic strontium content. The error for the radiogenic strontium content as calculated from the isotope dilution data was 0.35(±.07)ppm., that is, an error of 20%. The error in that calculated from the unspiked strontium data, on the other hand, was 0.36(±.02), an error of less than 6%. This is as predicted earlier in this chapter.

D. Error in final age calculation. It can be shown that for small values of the ratio, radiogenic Sr^{87}/Rb^{87}, such as have been encountered in the work on glauconite, the expression $\ln(1 + R/N)$ is essentially equal to R/N. The age formula may then be written:

$$t = 1/\lambda \times (R/N)$$

Substituting the values obtained for R and N in the above formula and using $1.39 \times 10^{-11}/yr$ for the decay constant,

$$t = (1/1.39 \times 10^{-11}/yr) \times \frac{0.36(\pm 0.02)}{65.0(\pm 1.3)}$$

$$= 395 \times 10^{6} \text{ years}$$

and the error in the age is equal to:

$$395 \times 10^{6}\sqrt{\frac{(0.02)^2}{(0.36)^2} + \frac{(1.3)^2}{(65.0)^2}}$$

$$= 25 \times 10^{6} \text{ years}$$

CHAPTER VI

RESULTS

The results of analyses of twenty-one glauconites are given in Tables XIX and XX. All results are given in parts per million. Ages were calculated using a decay constant of 1.39 x 10^{-11}yr-1, corresponding to a half-life of 50 x 10^9 years for the Rb^{87} decay. It will be noted that no rubidium analyses are given in Table XX. This is due to the fact that these six samples were analysed before it was realized that highly erroneous results could be attained as a result of rubidium contamination within the mass spectrometer. All rubidium analyses given in Table XIX were carried out after the rubidium had been isolated by ion exchange. These analyses are thought to be accurate to at least 3%. The normal strontium analyses given are also thought to be accurate to 3%. The errors for isotope dilution and isotope ratio determinations of radiogenic strontium are very close to the errors given for the respective isotope dilution and isotope ratio ages in the table.

Geologic ages of the glauconites analysed.

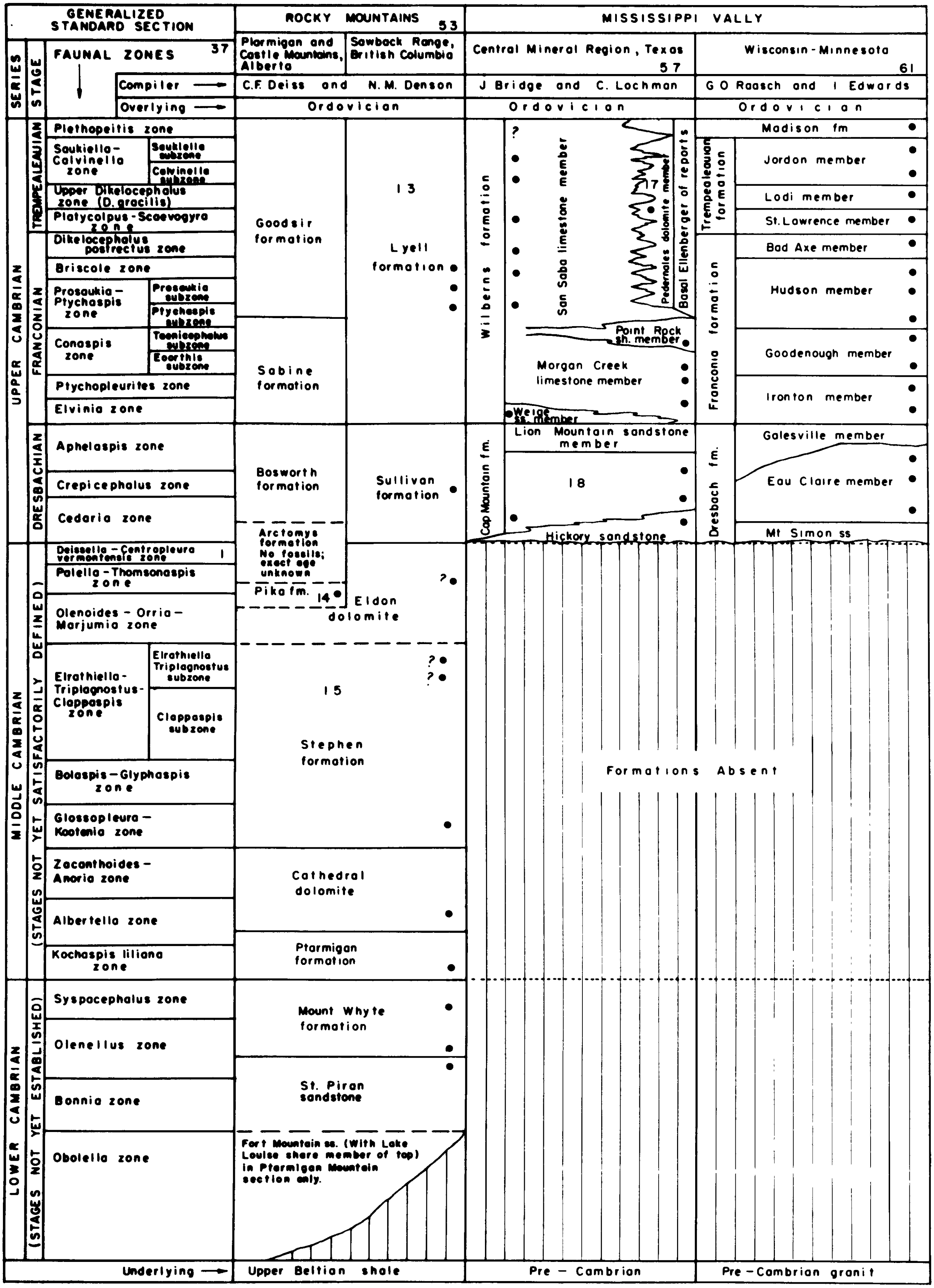
A. Cambrian samples: Measured ages of six Cambrian glauconites are given in Table XIX. Table XXI represents portions of the correlation chart set up by Howell et al (1944) for the Cambrian formations of North America. It will be noted that all of the Cambrian glauconites reported on here were ob-

TABLE XX

Sample	Location	Geologic Age	Normal Sr	Radiogenic I.D.	Sr I.R.
G1-1(a)	Lodi Shale, Wisc.	Upper Upper Cambrian	8.4	.31	-
G1-4	New Jersey	Upper Cretaceous	8.8	.11	-
G1-5	Mt.Whyte Fm. Alberta	Upper Lower Cambrian	321	.39	-
G1-6	Mt.Whyte Fm. Alberta	Upper Lower Cambrian	72.8	.29	-
G1-7(a)	Bridger Range,	Cambrian	213	.50	-
(b)	Montana		231	.68	±
G1-12(a)	Franconia Fm. Readstown,Wisc.	Upper Middle Cambrian	5.9	.37	.31

All concentrations given in ppm.

tained from formations actually shown upon Howell's chart with the single exception of the Murray Shale sample (G1-20). The Chilohowee Group, of which the Murray Shale is the uppermost member, is dated as being lowermost Cambrian by the United States Geological Survey in the Lexicon of Geologic Names of the United States. Other workers feel it to be Precambrian in age, in the Beltian series, e.g., Resser (1938). Howell's group has also placed the Chilhowee Group in the uppermost Precambrian. Actually, the whole problem is somewhat academic in that the placing



GENERALIZED STANDARD SECTION				ROCKY MOUNTAINS 53		MISSISSIPPI VALLY			
SERIES	STAGE	FAUNAL ZONES 37		Plarmigan and Castle Mountains, Alberta	Sawback Range, British Columbia	Central Mineral Region, Texas 57		Wisconsin-Minnesota 61	
		Compiler →		C.F. Deiss and N. M. Denson		J Bridge and C. Lochman		G O Raasch and I Edwards	
		Overlying →		Ordovician		Ordovician		Ordovician	
UPPER CAMBRIAN	TREMPEALEAUIAN	Plethopeitis zone		Goodsir formation	13 Lyell formation	Wilberns formation	? San Saba limestone member Pedernales dolomite member Basal Ellenberger of reports		Madison fm ●
		Saukiella-Calvinella zone	Saukiella subzone				●	Trempealeauan formation	Jordon member ●
			Calvinella subzone				●		●
		Upper Dikelocephalus zone (D. gracilis)					● 17 ●		Lodi member ●
		Platycolpus-Scaevogyra zone					●		St. Lawrence member ●
	FRANCONIAN	Dikelocephalus postrectus zone					●	Franconia formation	Bad Axe member ●
		Briscole zone			●		●		Hudson member ●
		Prosaukia-Ptychaspis zone	Prosaukia subzone		●				●
			Ptychaspis subzone	Sabine formation	●		●		●
		Conaspis zone	Taenicephalus subzone				Point Rock sh. member ●		Goodenough member ●
			Eoorthis subzone				Morgan Creek limestone member ●		●
		Ptychopleurites zone					●		Ironton member ●
		Elvinia zone					● ● Welge ss. member		●
	DRESBACHIAN	Aphelaspis zone		Bosworth formation	Sullivan formation	Cap Mountain fm.	Lion Mountain sandstone member	Dresbach fm.	Galesville member
		Crepicephalus zone			●		18 ●		Eau Claire member ● ●
		Cedaria zone					● ● ● Hickory sandstone		● Mt Simon ss
MIDDLE CAMBRIAN	(STAGES NOT YET SATISFACTORILY DEFINED)	Deissella-Centropleura vermontensis zone 1		Arctomys formation No fossils; exact age unknown	Eldon dolomite	Formations Absent			
		Palella-Thomsonaspis zone		Pika fm. 14 ●	? ●				
		Olenoides-Orria-Marjumia zone		Eldon dolomite					
		Elrathiella-Triplagnostus-Clappaspis zone	Elrathiella Triplagnostus subzone	15 Stephen formation	? ● ? ●				
			Clappaspis subzone						
		Bolaspis-Glyphaspis zone							
		Glossopleura-Kootenia zone			●				
		Zacanthoides-Anoria zone		Cathedral dolomite					
		Albertella zone			●				
		Kochaspis liliana zone		Ptarmigan formation	●				
LOWER CAMBRIAN	(STAGES NOT YET ESTABLISHED)	Syspacephalus zone		Mount Whyte formation	●				
		Olenellus zone			●				
		Bonnia zone		St. Piran sandstone	●				
		Obolella zone		Fort Mountain ss. (With Lake Louise share member of top) in Ptarmigan Mountain section only.					
		Underlying →		Upper Beltian shale		Pre-Cambrian		Pre-Cambrian granit	

Table XXI

of this group in either the Cambrian or Precambrian depends entirely on just how the base of the Cambrian is defined. It does seem quite probable though that the Chilhowee Group of sediments represents material that was deposited earlier than that deposited elsewhere in the country and thought to be basal Cambrian in age. In this sense, then, one would perhaps be justified in calling this group of sediments Precambrian.

The Mount Whyte Formation of southwestern Alberta and southeastern British Columbia, from which Gl-2, Gl-5, and Gl-6 were obtained, is dated at Upper Lower Cambrian by Howell et al (1944), Deiss (1936), and Rosetti (1951). The glauconite bearing layers in the Mount Whyte occur at its base. Howell states that Olenellus has definitely been identified in this formation.

One sample of glauconite from the Franconia Formation of Wisconsin and Minnesota was studied. Unfortunately, it is impossible to ascertain which member of the Franconia is represented by this glauconite, since the sample was incompletely labelled. However, we do know that this glauconite was deposited during the middle portions of Upper Cambrian time.

The Lodi Shale, from which Gl-1 was obtained, is placed by Howell in the Trempeleau Formation, although the United States Geological Survey considers it to be a member of the St. Lawrence Formation. In this case, we simply have two names for the same formation. The Lodi Shale is Upper Upper Cambrian in age.

Gl-15 and Gl-16 represent glauconites separated from two specimens of the Lion Mountain Sandstone member of the Riley Formation of central Texas. Gl-15 was obtained from drill core from a depth of over 5000', while Gl-16 was collected on the surface. The Riley Formation is equivalent to the Cap Mountain Formation. The geologic age of the Lion Mountain member appears to have been closely fixed on paleontologic grounds as Late Early Late Cambrian by Lochman (1938) and Palmer (1952).

B. Ordivician samples: The sample from Stenbrottet, Sweden (Gl-3 and Gl-11) occurs at the very base of the Ordovician in Sweden. The sample was collected only a few feet above Swedish kolm deposits known to be Upper Cambrian in age. Two other samples, from the Leningrad area of Russia, Gl-8 and Gl-21, were also analysed. Professor H.B. Whittington of Harvard University, who supplied the two samples, is presently examining well-preserved trilobites associated with them, and has assured the writer that the two are of Lower Ordovician age.

C. Devonian samples: Only one glauconite of Devonian age was obtained for this work. This sample was taken from the Carlisle Centre Formation of New York which is overlain by the Schoharie Formation or the Onondaga limestone in the Schoharie's absence, and underlain by the Esopus shale. According to the correlation chart for the Devonian strata of North America set up by Cooper et al (1942), the Carlisle Centre Formation would be Middle Lower Devonian in age.

D. Jurassic samples: The two Jurassic glauconites studied came from the Redwater Shale member of the Sundance Formation of the Laramie Basin, Wyoming. The Redwater Shale member is underlain by the Lak member and overlain by the Morrison Formation. The Redwater Shale member correlates faunally with the Curtis Formation of Utah, the Stump sandstone of eastern Idaho and westernmost Wyoming, the Swift Formation of Montana, and the "Upper Sundance" Formation of central Wyoming. Imlay (1947) places the Sundance as lowermost Upper Jurassic.

E. Cretaceous and Tertiary samples: Two of the samples studied, Gl-13 and Gl-14, are well dated geologically, Gl-13 is from the Navesink Formation, while Gl-14, collected from immediately above it, is from the Hornerstown Formation. Dorothy Carrol of the United States Geological Survey who collected the samples states that the Navesink is uppermost Cretaceous in age while the Hornerstown is Lower Eocene (private communication). Miller (1956), while agreeing that the Navesink is uppermost Cretaceous, states that the Hornerstown is Paleocene in age. However, the disagreement is slight for our purposes. The third sample, Gl-10, is subject to some doubt as to its actual age, since no location or formational name was given with it. However, it is almost certainly upper Cretaceous or Eocene in age.

F. Recent samples: The youngest glauconite studied (Gl-23) was obtained from a bottom sample taken in the Atlantic Ocean off Georges Bank. This glauconite is thought to be in the process of formation at the present time.

Previous attempts to set up absolute time scales: Table XXII illustrates a number of absolute time scales set up by various investigators for post-Precambrian time. The Table has been taken from Holmes (1947). These time scales have been set up mainly on the strength of a very few U/Pb age determinations. In nearly all cases, the minerals upon which the age determinations were made were of igneous rather than sedimentary origin. The age relationships of these minerals to nearby sediments were often vague. The differences among the various time scales of Table XXII are due primarily to two things:

(a) Agreement concerning the geological age of a given mineral or rock unit was not always unanimous.

(b) Improvements in the techniques of radioactive age determination gave rise to changes in the apparent ages of the minerals used.

Holmes, in 1947, revised his (1933) time scale on the basis of more refined U/Pb age determinations made possible by A.O. Nier's isotopic analysis of leads present in the uranium bearing minerals used. Up until that time, U/Pb ages were of a strictly chemical nature, that is, U-Pb concentrations were determined through chemical methods and isotopic analysis of lead was not carried out. In many cases, it was assumed that all lead present was radiogenic in origin. In other cases, atomic weight determinations on the lead allowed a fairly accurate correction from common lead to be made. The rapid development of mass spectrometry, however, including both isotope

TABLE XII

Systems	Barrell (1917)		Reeds (1931)		Holmes (1933)		Moore (1933)		Bullard (1944)	
Pleistogene	1-1.5	1-1.5	1	1	1	1	2	2	(5)	(5)
Pliocene	6-7.5	7-9			14	15			15	20
Miocene	12-14	19-23			17	32			25	45
Oligocene	16-16	35-39			10	42			18	63
Eocene	20-26	55-65		60	18	60		60	16	79
Cretaceous	65-85	120-150	68	128	68	128	65	125	76	155
Jurassic	35-45	155-195	30	158	30	158	32	157	23	178
Triassic	35-45	190-240	34	192	34	192	28	185	30	208
Permian	25-40	215-280	28	220	28	220	38	223	15	223
Carboniferous	85-90	300-370	65	285	65	285	86	309	47	270
Devonian	50-50	350-420	65	350	65	350	45	354	44	314
Silurian	40-40	390-460	25	375	25	375	27	381	18	332
Ordovician	90-130	480-490	65	440	65	440	67	448	47	379
Cambrian	70-110	550-700	70	510	70	510	105	553	47	426

Ages in millions of years

dilution and isotope abundance analysis, has enabled the investigator to measure U/Pb ages very accurately. Holmes' revised time scale, drawn up in 1947, is shown in Table XXIII. It will be noted that two scales are given in Table XXIII, labelled A and B. This was done because of some uncertainties in the geological ages of some of the minerals upon which the U/Pb age determinations were made. Holmes feels, however, that the B scale is to be preferred. Table XXIV represents a compilation of the U/Pb ages upon which Holmes' time scales (revised) are based.

TABLE XXIV

Sample	Geologic Age	207/206	206/238	207/235
A. Swedish kolm	Late-middle or early late Cambrian	800	377	440
B. Cyrtolite, Bedford, N.Y.	End of Ordovician (Taconic)	370	353	355
C. Cyrtolite, Bedford, N.Y.	End of Ordovician (Taconic)	412	337	345
D. Samarskite, Spinelli, Conn.	Late Devonian or Early Carboniferous	256	255	254
E. Pitchblende Joacimsthal	Late Carboniferous	214	225	221
F. Pitchblende Colorado	Beginning of Tertiary	-	57.3	55.1
G. Pitchblende Colorado	Beginning of Tertiary	-	59.8	61.2

Ages in millions of years

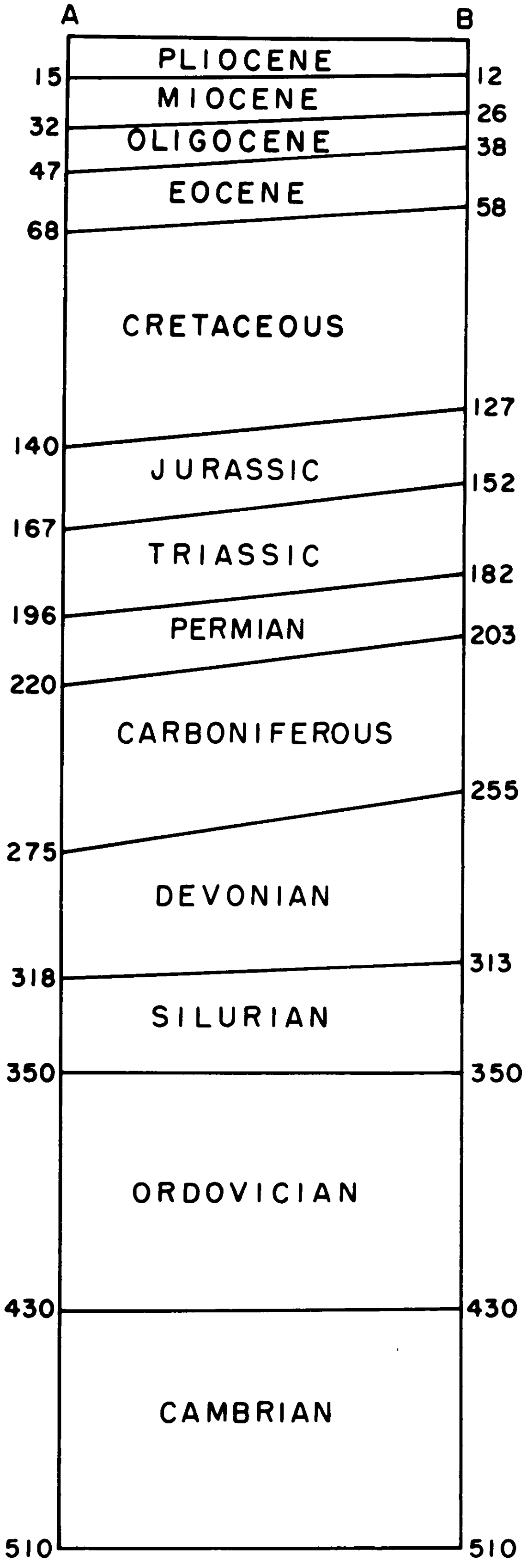


TABLE XXIII

TIME SCALES FOR POST-PRECAMBRIAN
AFTER HOLMES (1947)

It is to be noted in Table XXIV that in only one case, the Swedish kolm sample, was the age determination made directly on material of sedimentary origin. In all other cases, the minerals used were either from pegmatites or vein material associated with granites.

The ages obtained for the Swedish kolm sample show extreme discordancy. Wickman (1942), using data on the rates of diffusion of air and hydrogen through kolm material, calculated that average loss of radon would be 14.5% from a disk 7.5 cm. in thickness. Radon is a radioactive gas formed during the decay of U^{238} with a half-life of 3.8 days so that losses by diffusion can be appreciable. If radon is lost from a mineral being used for U/Pb age determination, there will be a corresponding decrease in the amount of Pb^{206} formed. This will result in measured 207/206 ages which will be too high and 206/238 ages which will be too low. The 207/235 age should be correct, provided of course that radon loss is the only process operative tending to change U/Pb ratios in the mineral other than the natural radioactivity. The kolm sample used by Nier for the U/Pb age determination given in Table XXIV was a disk between 5 and 10 cm. in thickness (kolm, a variety of oil shale, occurs as disk-like lenses in the alum shales of Sweden). Wickman found that by assuming a radon loss of about 17% in the sample analysed by Nier, the ages would become concordant at 440 million years. Wickman's correction for radon loss is illustrated in Figure IV. Holmes, on the basis of Wickman's work, assumed an age of 440 million years for the Swedish kålm deposits.

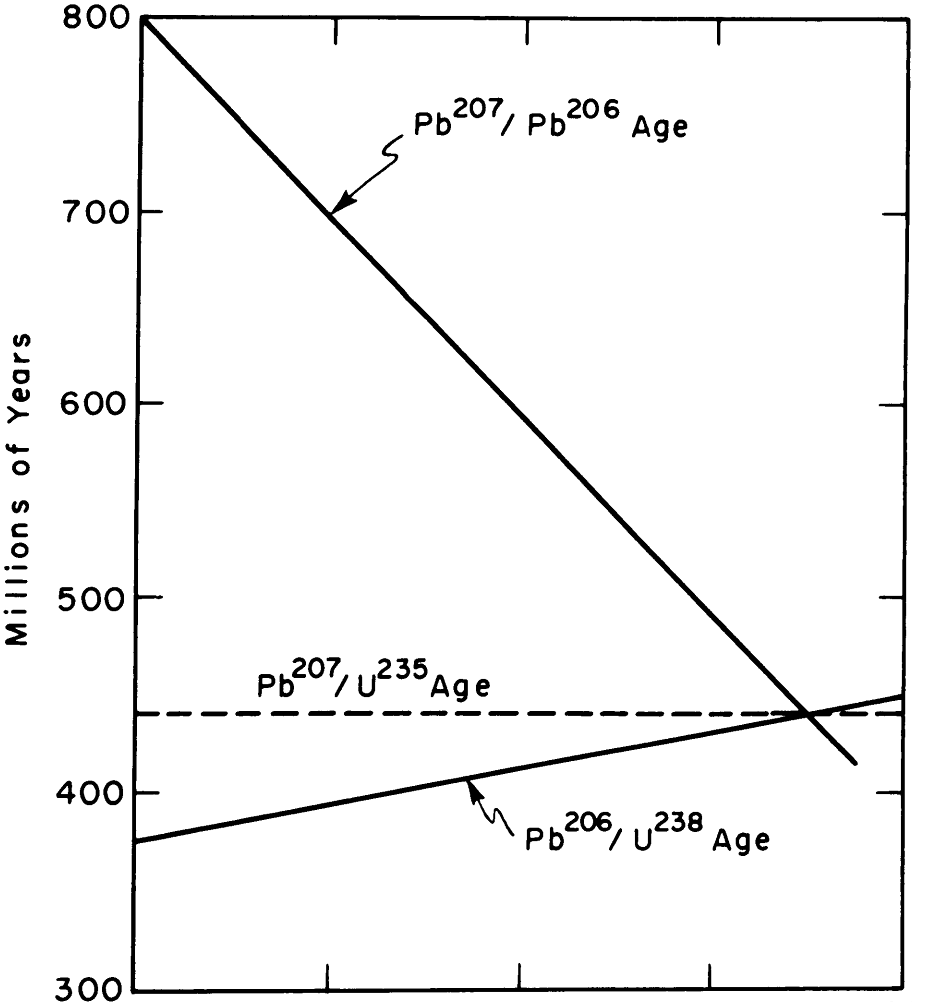


FIG. IV - CORRECTION FOR LOSS OF RADON. TAKEN FROM HOLMES (1947)

The ages obtained for the two cyrtolite samples from Bedford, New York, could be made concordant by assuming 0.7% and 2.9% radon loss respectively. The ages so obtained were 355 and 345 million years, and Holmes accepted an age of 350 million years for the close of the Ordovician.

In the case of the samarskite from Spinelli Quarry, Connecticut, beautifully concordant ages were obtained. However, some question existed as to the geological age of the granite with which the sample was associated. Most were of the opinion that the granite was intruded at the close of the Devonian during the Acadian orogeny. Others, however, expressed the possibility of a lower Carboniferous (Wichita) intrusion. Holmes feels that the granite represents intrusion at the close of the Devonian because no lower Carboniferous intrusives have been recognized in the region.

The Joachimsthal pitchblende has been dated at late Carboniferous or early Permian by geologists. On the basis of petrologic and tectonic evidence, however, Holmes feels that a late Carboniferous age is to be preferred.

The pitchblende samples from Colorado which were analysed came from veins genetically associated with the Laramide plutonic rocks of Colorado and Wyoming. The most widely accepted view is that the veins were formed at the close of the Cretaceous, but the possibility of an upper Paleozoic age has been recognized.

Lipson(1956) has recently completed studies on a suite of ten glauconites from the Tertiary of New Zealand. By measuring the concentration of K^{40} and radiogenic A^{40}, he was able to calculate ages for these glauconites. Lipson also determined the K/A ages of a lower Cretaceous (Albian) glauconite, a lower Cretaceous (Cenomanian) authigenic feldspar and a middle Devonian (Givetian) sylvite, all from western Canada. Lipson's results are shown in Table XXV.

TABLE XXV

Sample	Mineral	Location	Geologic Age	Measured Age $\times 10^{-6}$
47	Glauconite	New Zealand	M.Miocene	35.8(±2.0)
48	Glauconite	New Zealand	M.Miocene	30.2(±1.8)
56	Glauconite	New Zealand	M.Miocene	21.1(±1.5)
52	Glauconite	New Zealand	U.Oligocene	16.3(±1.0)
50	Glauconite	New Zealand	M.Oligocene	20.4(±1.2)
39	Glaconite	New Zealand	L.Oligocene	22.0(±1.5)
44	Glauconite	New Zealand	U.Oligocene	37.0(±2.6)
45	Glauconite	New Zealand	U.Oligocene	40.5(±2.8)
51	Glauconite	New Zealand	M.Paleozoic	49.2(±3.0)
38	Glauconite	New Zealand	L.Paleozoic	46.1(±2.8)
22	Feldspar	Crowsnest Volcanics, Alberta	M.Cretaceous	94.9(±4.7)
41	Glauconite	McMurray area, Canada	L.Cretaceous	142(±10)
32	Sylvite	Elk Point Formation, Saskatchewan	M.Devonian	285(±14)

Lipson's results, in general, agree well with Holmes' (1947) time scale and are extremely encouraging. Lipson used a branching ratio (A^{40}/Ca^{40}) of 0.11 in order to calculate the ages of the samples.

Wasserburg and Hayden (195$\overset{5}{6}$) measured the K/A ages of four authigenic minerals found in sedimentary rocks. Their results are given in Table XXVI. The ages given in Table XXVI have been calculated using a branch ratio of 0.11. Wasserburg and Hayden used a branching ratio of 0.085 in their published work, but this writer recalculated their ages using the higher value of the branching ratio in order that these results be comparable to those of Lipson.

TABLE XXVI

Sample	Mineral	Geologic Age	K^{40}/A^{40}Age
Franconia Fm.	Glauconite	Middle Upper Cambrian	460 x 10^6yrs
Dubuque Fm.	Feldspar	Upper Middle Ordovician	384
Marshalltown Fm.	Glauconite	Upper Cretaceous	71
Hornerstown	Glauconite	Eocene	52

Gentner *et al* (1954) measured the K^{40}/A^{40} age of a sylvite from the Lower Oligocene salt deposits of Germany. The measured age was 25(5,-2) million years, again in good agreement with Holmes' scale. Inghram et al(1950) obtained a K/A age of 89 million years for the Stassfurt sylvite. This is greatly at odds with Holmes' scale and indicates possible loss of argon.

Although a fairly large number of Rb/Sr ages have been measured, principally by the groups working at the Department of Terrestrial Magnetism and at M.I.T., they have been of little use in the setting up of a post-Precambrian time scale. This is so for two reasons:

(a) In many cases, the minerals analysed have been Precambrian in age.

(b) Minerals were taken from post-Precambrian igneous rocks whose relationships to paleontologically dated sediments were not clearly known.

One possible exception, however, is a lepidolite from the Pala Mine of southern California. This sample is thought by geologists to be either Upper Jurassic or Lower Cretaceous in age. Results of analyses of this lepidolite by both the D.T.M. and M.I.T. groups are shown in Table XXVII.

TABLE XXVII

Mineral	Location	Analyst	Sr*	Rb^{87}	Age($1.39x10^{-11}$ yr-1
Lepidolite	Pala, Calif.	D.T.M.	6.63	4120	116 x 10^6 yrs.
Lepidolite	Pala, Calif.	M.I.T.	6.47	3870	120 x 10^6 yrs.

Sr* represents radiogenic strontium. Analyses given in ppm.

It is felt that the measured ages cited in the foregoing paragraphs represent those most suitable for the construction of an absolute time scale for the Paleozoic, Mesozoic and Cenozoic eras. These ages are combined graphically in Figure V. The measured ages have been plotted against the B time scale set up by Holmes in 1947. The solid line in Figure V represents a plot of the four U/Pb ages used by Holmes (see Table XXIV) in setting up the time scale. The various other points represent the ages measured by Lipson (1956), Wasserburg and Hayden (1955), the Pala lepidolite values obtained by the D.T.M. and M.I.T. groups,

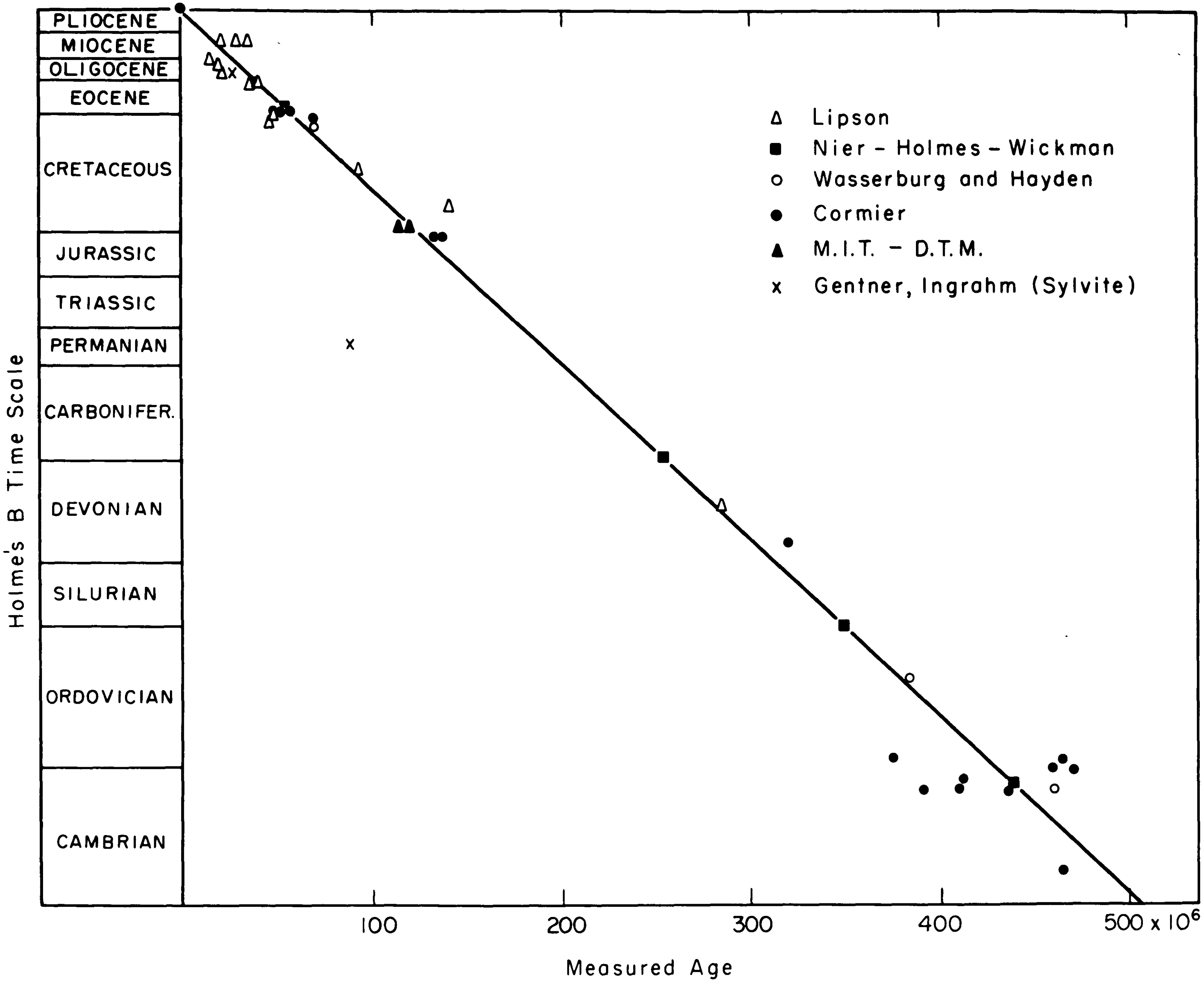

PLIOCENE
MIOCENE
OLIGOCENE
EOCENE
CRETACEOUS
JURASSIC
TRIASSIC
PERMANIAN
CARBONIFER.
DEVONIAN
SILURIAN
ORDOVICIAN
CAMBRIAN
Holme's B Time Scale
△ Lipson
■ Nier - Holmes - Wickman
○ Wasserburg and Hayden
● Cormier
▲ M.I.T. - D.T.M.
x Gentner, Ingrahm (Sylvite)
100
200
300
400
500 x 10^6
Measured Age

Fig.V

Gentner's (1954) sylvite age, and the Rb/Sr glauconite ages reported on here.

The most striking feature of Figure V is the rather remarkable agreement between Holmes' time scale and the ages measured by other workers. It should be remembered that the ages plotted represent work done using three different naturally occurring radioactive decay schemes by a number of workers in different laboratories, and no known data has been excluded. Of the 36 measured ages plotted in Figure V, neglecting of course the four U/Pb ages used to construct the time scale, 28 fall on, or very close to, the line representing Holmes' scale. Of the 8 which fall off the line by amounts greater than a single standard error, six are Rb/Sr glauconite ages reported on here for the first time. One is a K/A glauconite age by Lipson, and the other is Inghram's K/A sylvite age. Ten Rb/Sr ages fall on the line or within a single standard error of it. None of the ages plotted fall off the line by as much as two standard errors, except Inghram's age for the Stussfurt sylvite.

Evaluation of the Rb/Sr glauconite ages. Sixteen Rb/Sr glauconite ages are being reported on here at this time. The six ages which appear to show significant lack of agreement with other ages cited here are:

(a) One age measured for the Stenbrottet, Sweden sample (Gl-11).

(b) Three ages measured for the two Lower Ordovician samples from the Leningrad area of Russia (Gl-8 and Gl-16).

(c) Two ages measured for the two Upper Cambrian samples from the Riley Formation of central Texas (Gl-15 and Gl-16).

The Rb/Sr ages plotted in Figure V represent only "isotope ratio" ages, that is, ages in which the radiogenic strontium content was calculated on the basis of analysis of pure, unspiked strontium extracted from the glauconite. "Isotope dilution" ages were, however, also obtained in all but one case. Figure V has been limited to "isotope ratio" ages because of their much greater accuracy. In the case of the Swedish glauconite, however, age determinations were made on two samples,, Gl-3 and Gl-11, as can be seen in Table XIX. Three ages were obtained, only one of which was an "isotope ratio" age. The two isotope dilution ages obtained, however, agree well with the single isotope ratio age, as can be seen in Table XIX. Of the two isotope dilution ages, one agrees almost exactly with the isotope ratio age, 375 as compared to 380 million years. This isotope dilution age was obtained for Gl-3 and has a small standard error (10%) as compared with most isotope dilution ages. The other isotope dilution age, that obtained for Gl-11, is significantly higher than the isotope ratio age obtained for the same sample (420 m.y.) but the standard error for this isotope dilution age was quite large (20%).

In the case of the two Lower Ordovician samples from Russia, Gl-8 and Gl-21, three isotope ratio ages were obtained. Two of the three were on Gl-8, where an unleached and a leached fraction were each analysed. The reasons for this will be discussed further on in this work. At any rate, the three isotope ratio ages obtained are in excellent agreement. All three ages indicate a Lower or Middle Cambrian age rather than Lower Ordovician.

Two isotope ratio ages were obtained for the two samples from the Riley formation of Central Texas, one for each. These two ages agreed well with one another. Moreover, a glance at Table XIX will show that the two isotope dilution ages obtained for these samples are, also in excellent agreement with the isotope ratio ages.

There are a number of possible reasons which might be advanced to explain discrepancies in the measured Rb/Sr ages of glauconites. The first that comes to mind is analytical error, that is, error introduced during the analysis of the glauconite. This explanation does not appear tenable, however, in the case of the six apparently discrepant ages just discussed. Thus, in the case of the Russian samples, three ages in complete agreement were measured; two ages were obtained for two different samples of the Riley Formation glauconite that again showed good agreement; and for the Swedish sample, one and possibly two isotope dilution ages were found to agree very closely with the single isotope ratio age obtained. If analytical errors were responsible for the discrepancies, then we would not expect concordancy between ages of samples from the same formation or closely related horizons. For this reason, it is concluded that analytical errors are not responsible for the apparently discrepant ages.

It should be noted that of the six apparently erroneous ages, the Russian samples appear to be too old, while the Swedish and Riley formation ages appear to be too young. It is rather difficult to explain the apparent discrepancies on the basis of post depositional changes in the glauconites, since if the variations were due solely to such influences, more than one process would have to be operative. Possible reasons for measured Rb/Sr ages being too old are:

(a) During the glauconite's history, rubidium was leached preferentially with respect to strontium.

(b) Glauconite may form as the result of alteration of older, detrital, rubidium-rich minerals, such as biotite or muscovite. If this were the case, and the mineral undergoing alteration contained significant amounts of radiogenic strontium which was not entirely removed during the alteration, the measured age of the glauconite would be too high. In order to test this possibility, glauconite known to be forming today as the result of alteration of detrital, rubidium-rich minerals should be analysed. Thus, glauconite currently forming in Monterey Bay, California, has been shown by Galliher (1935) to be an alteration product of biotite currently being eroded and carried into the bay from adjacent granites. Analysis of glauconite and biotite from the bottom sediments of the bay should disclose whether or not radiogenic strontium originally present in the biotite is removed during the alteration process.

(c) The presence of older, detrital, rubidium-rich minerals as impurities in the glauconite sample analysed could lead to measured ages which were too old. This possibility is not likely, however, since microscopic examination of the glauconite sample was made before it was used for age determinations. The presence of such contaminating minerals would have been disclosed to the analyst.

(d) Microscopic examination of glauconites separated from sediments has led some investigators to conclude that the glauconite represents reworked and redeposited material. If this occurred, the measured age of the glauconite would be greater than the true age of the sediment in which the glauconite occurred. This does not appear to be a reasonable explanation in the case of the two Russian samples, however, since microscopic examination of the separated glauconites showed most of the grains to be casts of shells, many of them perfect in every detail. Erosion and redeposition of these grains would almost certainly lead to complete destruction of such fine and delicate structure.

Processes operative in nature that would lead to measured Rb/Sr ages that were too young are somewhat more difficult to visualize. There is the possibility, of course, that radiogenic strontium might be leached from the mineral utilized, resulting in ages that were erroneously young. Another possibility is that rubidium has been added to the mineral since it was originally formed. This would lead to an erroneously young age because, in the age calculation, it is assumed that the concentration of Rb found in the mineral has not changed since the mineral was formed.

Local variations in the relative abundances of the stontium isotopes present in the environment of formation of the mineral could give rise to measured ages which were either too old or too young, depending upon the direction taken by the variations. Thus, if the abundance of Sr^{87} present in the strontium included in a glauconite at the time of its formation differed significantly from that in so-called normal or common strontium, the calculated age would be in error because, in the calculation, the abundance of Sr^{87} assumed to have been present at the time of formation of the mineral would be incorrect. Numerous analyses of strontium extracted from limestone, glauconite, celestite, etc., have failed to show significant variations in the relative abundances of the strontium isotopes which are not radiogenic in origin. Since the non-radiogenic isotopes of strontium fail to show such variations, it would be necessary that the mineral form in an environment in which the strontium present differed only in its abundance of the mas 87 isotope. It is difficult to accept such a mechanism, particularly in the case of glauconite. Glauconites have formed in the sea, an environment which we would expect to be quite homogeneous. Samples of strontium taken from sea water and high strontium, low rubidium materials of marine origin have failed to show any significant variations in the abundance of strontium 87 (See Table XII). In order to test this hypothesis as a possible means of explaining the high ages obtained for the two Russian samples, strontium was extracted from a pure sample of the limestone with which Gl-8 was associated (Iswos limestone) and this was analysed isotopically. It is to be expected of course that such strontium would be representative, isotopically, of the strontium included in Gl-8 at the time of its formation. The isotope analysis disclosed that this strontium was normal in every respect (see Table XII). In summary then, local variations in the relative isotopic abundance of Sr^{87} does not appear to be a satisfactory explanation of discordant Rb/Sr glauconite ages. The reasons for this conclusion are.

(a) Analysis of strontium extracted from sea water and materials of marine origin in which the ratio Sr/Rb is high fails to show any significant variation in the relative abundances of the isotopes of strontium (See Table XII).

(b) Analysis of strontium extracted from a number of glauconites fails to show significant variations in the relative abundances of the non-radiogenic isotopes (see Table XIII). This would tend to eliminate such a process as natural fractionation from giving rise to the Sr^{87} variations, since it would result in changes in the relative abundances of all the isotopes.

(c) Glauconites have formed in the sea, an environment which appears to be homogeneous with respect to the relative abundances of the strontium isotopes.

Thus far in the discussion of the results obtained from the Rb/Sr analyses of glauconites, the possibility has not been suggested that the geological ages assigned to the six glauconites in question may be in error. If one accepts this as an explanation for discordant ages of glauconite samples, he must be prepared to conclude that geologic ages assigned on the basis of paleontology can be erroneous. In some cases this is no doubt true. However, the six ages in question here were obtained for materials that have been dated paleontogically in what might be called rigorous fashion. By this is meant that there does not appear to be any question as to their age from the viewpoint of the paleontologist. Again, the majority of the ages cited in Figure V are in complete agreement with the ages assigned on the basis of paleontology, and it would not appear reasonable to assume that for those ages which show discrepancies, paleontologic evidence had led to the assignment of erroneous geologic ages.

Conclusions.

1. Glauconite Rb/Sr ages appear to be, in general, reasonable. More than half the ages measured agree well with ages obtained by other investigators using other methods of age determination. In some cases, the glauconite Rb/Sr ages appeared to be somewhat too high or too low. Good agreement between the ages measured for a number of such samples from the same area or formation indicates that the discrepancies are not due to

analytical errors, and must therefore be due to processes operative subsequent to or during the formation of the glauconite.

2. Although some glauconite Rb/Sr ages may be in error, as the result of natural processes, the degree of error in most cases is not excessively high. It is felt that in all probability, glauconite Rb/Sr ages will enable the petroleum geologist and stratigrapher to determine with considerable confidence the period in geologic time to which a nonfossiliferous stratum should be assigned.
3. The time scale set up by Holmes (1947) for the Paleozoic, Mesozoic, and Cenozoic eras, and known as the Holmes B time scale, appears to correlate very closely with age determinations made on a variety of materials by several workers. It is felt that this time scale is, in all probability, free of serious error, and any changes in this time scale as a result of further absolute age determinations will probably be of only a minor nature.
4. The relative abundances of the strontium isotopes in sea water have remained essentially constant throughout post-Precambrian time.
5. The mineral glauconite contains from 180 to 320 parts per million rubidium. The near constancy in rubidium content of glauconites of all ages and from all over the world is in sharp contrast to the exceedingly variable rubidium content of such minerals as biotite (50-2300 ppm) (Herzog, <u>et al</u>, 1956). This probably stems from the fact that glauconites have all formed in a common environment, the sea.

6. In order that accurate rubidium determinations may be made in the mass spectrometric analysis of glauconite, it is necessary that the rubidium be isolated, e.g., by ion exchange, before being placed on the filament. Otherwise, significant rubidium contamination may be introduced on the filament itself as a result of memory effects within the mass spectrometer.

7. Isotopic analysis of pure, unspiked strontium extracted from glauconite allows a much more accurate determination of radiogenic strontium than does the analysis of the spiked strontium in the isotope dilution run. Because of the small amounts of radiogenic strontium in glauconites, this should be made standard procedure in Rb/Sr age determinations on glauconite.

Recommendations for future research.

A. It is suspected that a major portion of the normal strontium contents found in the glauconites thus far analysed is present, not in the glauconite itself, but in other minerals, present as impurities, associated with it. It is felt that in most cases, this additional strontium is present in the carbonates. Leaching of the sample with HCl or some other reagent would get rid of much of the contaminating strontium. If it can be shown that such leaching does not affect the measured age of the glauconite, then it should be made standard procedure. The decrease of normal strontium content thus achieved will result in significantly more accurate radiogenic strontium determination. This was tried in the case of Gl-8, the Iswos limestone sample. The glauconite sample was split into two portions. Bl-8(a) was leached with 1.5N HCl for three minutes before analysis. Gl-8(b) was not leached. The leached fraction was found to contain 4.2ppm normal strontium, while the unleached was found to contain 28.9ppm or more than seven times as much. The leaching process did not appear to have any effect on the measured ages of the two samples (See Table XIX). However, further experiments along thesellines are needed.

B. A single, large sample of glauconite should be divided into a number of fractions, and age determinations should be made on each. An understanding of run-to-run precision would thus be obtained.

C. Age determinations should be made on a number of glauconite samples collected from the same glauconitic horizon. In this way, an idea of sample-to-sample reproducibility would be gained.

D. Subsurface samples of glauconite obtained from drill cores should be analyzed and the ages obtained compared with those obtained from surface outcrop equivalents. The affects of of weathering on measured ages could then be evaluated. This was done in the case of the two samples from the Riley Formation, Texas, and the ages obtained were in good agreement.

E. If possible, the ages of glauconites which have undergone folding and metamorphism should be measured and compared with ages obtained from glauconites known to be of the same geologic age but which have not undergone strong metamorphism.

F. As well as measuring the Rb/Sr age of a glauconite, its K/A age should also be determined. For each sample, two completely independent ages would be obtained.

G. Glauconites known to be forming at present as the result of alteration of older, rubidium-rich minerals such as biotite should be analysed in order to determine whether or not any radiogenic strontium present in the parent material is carried over into the resulting glauconite. If this were found to be so, then we would know that at least some glauconites are not suitable for Rb/Sr age determinations.

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BIOGRAPHICAL NOTE

The author was born in Truro, Nova Scotia, November 9, 1930. He was graduated from St. Vincent's Boys' High School, St. John, New Brunswick, in 1947. He obtained his Senior Matriculation certificate from St. John High School in 1948. He entered St. Francis Xavier University, Antigonish, Nova Scotia, in September, 1948 and received an engineering certificate in May, 1950, and was graduated as a Bachelor of Science in geology in May, 1951. He entered the Massachusetts Institute of Technology in September, 1952.

The author was married to Marie Cantwell in 1955. He has a brother, Paul, who is employed with the Ontario Hydro Commission as an electrical engineer. A sister, Eileen, teaches in the public schools of St. John, New Brunswick.

The writer's professional experience includes three summers as exploration geologist for mining companies, one summer with the Geological Survey of Canada, and one summer with the Canadian Topographic Survey. He was a research assistant during his entire stay at M.I.T. As a research assistant, in addition to two years spent in mass spectrometry, the author undertook research in the petrofabric analysis of carbonate rocks under the direction of Professor H.W. Fairbairn, and optical spectrographic analysis of coal ashes under the direction of Professor W.L. Whitehead and Professor W.H. Dennen.

The author delivered a paper, entitled "Rb/Sr Age Studies on Glauconites" at the May, 1956 meeting of the American Geophysical Union.