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# Geochronology\*

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## Contents

Introduction.....	2
I. Basic Principles.....	2
II. $K^{40}$ -Ar <sup>40</sup> ( $K^{40}$ -Ca <sup>40</sup> ).....	5
A. General Description.....	5
B. Analytical Measurements.....	5
C. Evaluation.....	6
III. Rb <sup>87</sup> -Sr <sup>87</sup> .....	8
A. General Description.....	8
B. Analytical Measurements.....	8
C. Evaluation.....	9
IV. $U^{238}$ -Pb <sup>208</sup> , $U^{235}$ -Pb <sup>207</sup> , $Th^{232}$ -Pb <sup>208</sup> , $Pb^{207}$ -Pb <sup>206</sup> .....	14
A. General Description.....	14
B. Analytical Measurements.....	14
C. Evaluation.....	15
V. Dating Pb Minerals by means of their Isotopic Constitutions.....	21
A. Theory and Models for Pb-mineralization.....	21
B. Anomalous Leads.....	26
C. Criteria.....	27
VI. Concordance, Discordance and Updating.....	30
A. Violation of Basic Criteria.....	30
B. Differential Updating of Minerals.....	32
C. Two Examples of the Effects of Metamorphism.....	34
D. General Comments.....	40
VII. The Dating of Sedimentary Rocks.....	41
A. Evaluation of Materials.....	41
B. Applications.....	45
References.....	46

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## Introduction

Geochronology may be considered to be the study of the time relationships of geological materials and processes by means of isotopic variation caused by the disintegration of naturally-occurring radioactive nuclides. Geologists have been long concerned with reconstructing a sequence of geologic events for both local and worldwide phenomena. The use of the law of superposition, intrusive relationships and fossil correlation have served well and continue to serve, but are subject to a number of deficiencies. For example, if the earth is about 4500 million years old, it appears that less than 15 per cent of geologic time is available for reasonable time correlation using fossils. In addition, large areas of unfossiliferous rocks are present, and the relative rate of consecutive geologic process can be estimated only in very special cases. With the discovery of radioactivity, a new time-measuring factor was made available to the geologist. It was found that the rates of decay of radioactive nuclides remain essentially unchanged regardless of their geologic environment. If the amount and rate of decay of the radioactive parent nuclide and the amount of the radiogenic daughter nuclide can be determined, the time taken to accumulate the measured amount of radiogenic daughter may be calculated. This time represents, for example, the time elapsed since a mineral containing the parent crystallized, providing the mineral was a chemically-closed system from the time of its formation. There are present in nature a number of long-lived radioactive nuclides, each of which may be regarded as the works for a potential "nuclear clock". These nuclides are distributed in various geological environments, but their utility is limited by a number of factors. Notwithstanding their limitations, these nuclear "clocks" are applicable in many instances where little other means of time correlation are available. Though the understanding of the drawbacks and application of these "clocks" is yet incomplete, they have been used in many ways already.

### I. Basic Principles

Assume there is a certain amount of a radioactive nuclide such as  $\text{Rb}^{87}$ ,  $N_0$  atoms, incorporated in a phase (mineral) at some past time,  $t_0 = 0$ , in geologic time. After a lapse of time up to the present time,  $t$ , there are only  $N$  atoms of  $\text{R}^{87}$  left. For  $\text{Rb}^{87}$  with the decay scheme  $\text{Rb}^{87} \rightarrow \text{Sr}^{87} + \beta^-$ :

$$N_0^{\text{Rb}^{87}} - N_t^{\text{Rb}^{87}} = N_t^{\text{Sr}^{87}} \quad (1)$$

From the fundamental equation for radioactive decay:

$$N_t^{\text{Rb}^{87}} = N_0^{\text{Rb}^{87}} e^{-\lambda t} \quad (2)$$

where  $\lambda$  is the decay constant for  $\text{Rb}^{87}$ .

Rearranging (2),

$$N_0^{Rb^{87}} = N_t^{Rb^{87}} e^{\lambda t} \quad (3)$$

and substituting in (1)

$$N_t^{Sr^{87}} = N_t^{Rb^{87}} (e^{\lambda t} - 1).$$

Solving for t,

$$t = \frac{1}{\lambda} \left( \frac{N_t^{Sr^{87}}}{N_t^{Rb^{87}}} + 1 \right). \quad (4)$$

The general relation, corresponding to this case, is

$$t = \frac{1}{\lambda} \ln \left( \frac{D}{P} + 1 \right). \quad (5)$$

Where D is amount of daughter and P is the amount of parent. When  $P_t = 1/2 P_0$ , or  $P_t = D_t$ ,

$$t = \frac{\ln 2}{\lambda} = t_{\frac{1}{2}}, \text{ the half-life of the parent.}$$

If the amount of parent and daughter isotopes can be determined and  $\lambda$  is known, one may calculate t, the time at which the closed system formed (or mineral crystallized).

There are a number of criteria which must be fulfilled, however, before much significance may be attached to any such calculated number, or date (RANKAMA, (1954) p. 110).

#### Fundamental requirements in geochronology

1. The rate of decay of the radioactive nuclide must be known, i.e. must be accurately known and of favourable magnitude.
2. Sampling must be representative of a known geologic phase.
3. Analytical measurements must be able to be made accurately (essentially, parent and daughter determination).
4. Ideally, no daughter (or intermediate decay product as in the radioactive series of  $U^{238}$  to  $Pb^{206}$ ) should be incorporated or present in the phase to be dated at the time of its formation. Generally, the amount of "contaminant" daughter must be able to be determined and a correction made.
5. No gain or loss of either parent nuclide or daughter should occur after the phase (to be dated) has once formed a closed system.
6. When an abundance ratio is used to determine the amount of the parent nuclide in the presence of the normal isotopes, the isotopic composition of the element in question must be known and constant, or essentially so, in the lithosphere.

The isotope abundance ratios for the parent nuclides of the important "nuclear clocks" have been shown to be essentially constant. Criterion number 6 will not be further discussed. Let us look at the possibilities for "nuclear

Table I  
Naturally Radioactive Nuclides

Radioactive Nuclide	Daughter	Half Life, Yrs.	Percentage Abundance in the Element
C <sup>14</sup>	N <sup>14</sup>	5730	-
K <sup>40</sup>	89.0% Ca <sup>40</sup> 11.0% Ar <sup>40</sup>	1.27 × 10 <sup>9</sup>	0.0119
Rb <sup>87</sup>	Sr <sup>87</sup>	4.7 × 10 <sup>10</sup>	27.85
In <sup>115</sup>	Sn <sup>115</sup>	6 × 10 <sup>14</sup>	95.77
Te <sup>130</sup>	Xe <sup>130</sup>	10 <sup>21</sup>	34.49
La <sup>138</sup>	Ce <sup>138</sup> Ba <sup>138</sup>	7 × 10 <sup>10</sup>	0.089
Sm <sup>147</sup>	Nd <sup>143</sup>	6.7 × 10 <sup>11</sup>	15.07
Nd <sup>150</sup>	Pm <sup>150</sup>	2 × 10 <sup>15</sup>	5.60
Lu <sup>176</sup>	33% Hf <sup>176</sup> 67% Yb <sup>176</sup>	2.4 × 10 <sup>10</sup>	2.6
Re <sup>187</sup>	Os <sup>187</sup>	4 × 10 <sup>12</sup>	62.93
Bi <sup>209</sup>	Tl <sup>205</sup>	2.7 × 10 <sup>17</sup>	100
Th <sup>232</sup>	Series to Pb <sup>208</sup>	1.39 × 10 <sup>10</sup>	100
U <sup>235</sup>	Series to Pb <sup>207</sup>	7.07 × 10 <sup>8</sup>	0.71
U <sup>238</sup>	Series to Pb <sup>206</sup>	4.51 × 10 <sup>9</sup>	99.29

clocks" among the naturally-occurring radioactive nuclides and in the light of the first five requirements (see page 3).

Applying criteria 1 and 3, many of the radioactive nuclides in Table I are seen to be unsuitable for use as nuclear "clocks". That is, uncertainties in the mode of decay or too long half-lives serve to eliminate a number of the nuclides from immediate consideration. If the age of the earth is  $4.5 \times 10^9$  years, and the half-life of a radioactive nuclide is  $4.5 \times 10^{11}$  years, then the original parent has decayed to give only 1/100 as much daughter. Alternately, if the half-life of the parent is  $4.5 \times 10^7$  years, only 1/100 of the parent remains to be determined. Outside of these limits of a 100-fold factor of the age of the earth, either the amount of daughter or the amount of parent becomes very small and is usually difficult to determine. Thus, In<sup>115</sup>, Te<sup>130</sup>, Nd<sup>150</sup> and Bi<sup>209</sup> have such large half-lives that too small amounts of daughter will be available for determination. Radioactive nuclides whose half-lives are  $< 4.5 \times 10^7$  years have essentially disappeared over geologic time. Difficulties in determining the known relative proportions of Bi<sup>138</sup> and Ce<sup>138</sup> eliminate La<sup>138</sup>. The determination of a small amount of Nd<sup>143</sup> among rare earth elements and of Hf and Yb in rare earth minerals and the scarcity of Re-rich minerals eliminate these possibilities for present general use. C<sup>14</sup>, K<sup>40</sup>, Rb<sup>87</sup>, Th<sup>232</sup>, U<sup>235</sup> and U<sup>238</sup> remain as good possibilities and, indeed, these nuclides have been extensively investigated and utilized. C<sup>14</sup>, since it is constantly generated by cosmic ray bombardment of N<sup>14</sup> in the upper atmosphere, is present in the young biosphere despite its short half-life. Taking only the suitable nuclides with half-lives within a factor of one hundred of the age of the earth, the remaining possibilities will be considered with reference to the fundamental criteria for a good nuclear "clock".

II.  $K^{40} - Ar^{40}$  ( $K^{40} - Ca^{40}$ )

A. General Description

This nuclear "clock" is based on the decay of  $K^{40}$  to  $Ar^{40}$  and  $Ca^{40}$ . The decay scheme is given in Fig. 1. The parent-daughter pair  $K^{40}-Ca^{40}$  is seldom accurately applicable for dating since criterion 4. (initial absence of significant amounts of the daughter) is rarely fulfilled. The ubiquity of  $Ca^{40}$ , even in minerals where no Ca-diadochy is involved, generally makes sufficiently accurate correction for contaminant daughter too difficult except for certain pure micas and salts (as lepidolite and sylvite). The branch of the decay scheme to  $Ar^{40}$  is more suitable as regards daughter contamination, since Ar possesses little tendency to be incorporated in any but a few special minerals. The fact that potassium is a major crustal component and is therefore widespread in its occurrence makes the K-Ar "clock" capable of wide possible application. In addition, the rare gas, Ar, is relatively easily extracted from minerals and purified, and its determination is feasible down to very small amounts.

B. Analytical Measurements

Potassium may be determined by a variety of chemical and instrumental methods in the range 1-15 per cent  $K_2O$ . Below one per cent  $K_2O$  and down to one part per million  $K_2O$ , stable isotope dilution (INGHRAM, 1954) may be used. The  $K^{40}$  content of the sample is then calculated from the isotopic abundance of  $K^{40}$  in crustal potassium (0.0119 atomic per cent (NIER, 1950)).

Argon plus contaminant gases such as  $N_2$ ,  $H_2$ ,  $CO_2$  and hydrocarbons are released from the samples by fusion with or without a flux (as NaOH) in a highly-evacuated extraction train. The liberated gases are mixed with a known amount of  $Ar^{38}$  of known isotopic purity - the so-called "spike". Contaminant gases are removed by chemical "gettering" and liquid-air traps, leaving Ar (plus small amounts of other rare gases) of high purity. The extracted argon, mixed with spike argon, is then passed into a mass spectrometer for determi-

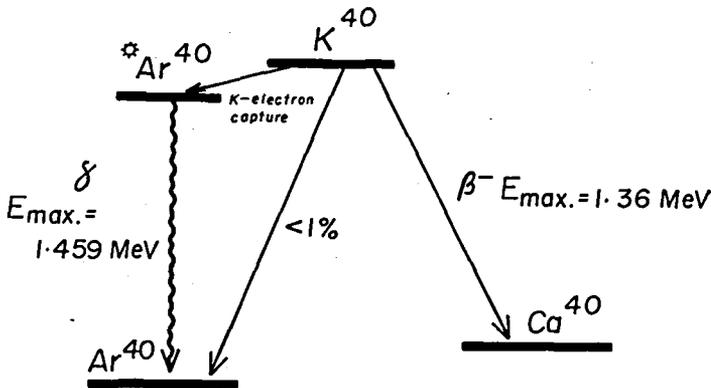


Figure 1. The decay scheme of  $K^{40}$ .

nation of the relative atomic proportions of Ar<sup>36</sup>, Ar<sup>38</sup> and Ar<sup>40</sup>. The extracted argon also contains some air argon contamination. Ar<sup>36</sup> is utilized as a tracer for air argon contamination, and after correcting for the amount of Ar<sup>40</sup> contamination, the amount of radiogenic argon may be computed from the measured isotope ratios.

### C. Evaluation

#### 1. Decay Constants

To provide a common basis for comparison of K-Ar dates, almost all workers now use the constants adopted by Aldrich and Wetherill (4):

$$\begin{aligned} \text{(electron-capture)} \lambda_e &= 5.85 \times 10^{-11} \text{yr.}^{-1} \\ \text{(}\beta\text{-decay)} \lambda_\beta &= 4.72 \times 10^{-10} \text{yr.}^{-1}. \end{aligned}$$

AS ALDRICH and WETHERILL (4) have shown, the error in a computed date is much more sensitive to an error in  $\lambda_e$  than a comparable error in  $\lambda_\beta$ . The quoted value of  $\lambda_e$  is believed to be within 5 per cent of the true value, while the spread in values for  $\lambda_\beta$  is about 10 per cent. Other factors being equal, the errors in the decay constants for K<sup>40</sup> give rise to uncertainties in the computed dates of from 5 to about 8 per cent. These uncertainties are of importance when dates from other nuclear "clocks" are compared, but do not enter in when relative K-Ar dates are being considered.

#### 2. Analytical Sensitivity

If  $t = 10^5$  years,  $\text{Ar}^{40}/\text{K}^{40} = 0.000067$ ; and if  $t = 10^{10}$  years,  $\text{Ar}^{40}/\text{K}^{40} = 20.7$ . For potassium minerals containing at least two per cent K<sub>2</sub>O, the ratio  $\text{Ar}^{40}/\text{K}^{40}$  may be determined down to 0.00005 (even less in special cases) with modern techniques (cf. EVERNDEN, 1959). Almost all of geologic time is within the range of the K-Ar "clock", and it is by far the most widely applicable "clock" in Mesozoic time.

A measure of the ability of the K-Ar "clock" to furnish analytically reliable data is given by interlaboratory comparison of determined Ar<sup>40</sup> and K. Various numbers of such checks have been made and show in general that Ar<sup>40</sup>-determinations may be reproduced to about  $\pm 1$  per cent on Precambrian samples. Most laboratories can reproduce their own potassium values to within 1-2% on replicate determinations, but up to 6 per cent variation in potassium values may occur between various laboratories. The exact causes of such variation in K-values have not been found, and it seems strange that the much smaller amount of Ar<sup>40</sup> in K-minerals may be more reliably determined!

#### 3. Contaminant Daughter

All minerals contain some trapped or occluded nonradiogenic Ar<sup>40</sup>. This argon is probably somewhat variable as regards isotopic composition, but for the purposes of correction its isotopic composition is taken to be that of present day air argon. That this is a reasonably valid assumption is shown by the fact that very young cogenetic minerals give the same dates although the

contaminant "air" argon corrections vary from 10-90 per cent. It might be asked whether or not Precambrian contaminant argon is likely to have the same isotopic composition as modern air argon. This error factor is not critical since in most Precambrian samples the contaminant  $\text{Ar}^{40}$  correction is only 1-2 per cent of the total  $\text{Ar}^{40}$ . Errors in the correction then contribute little to the overall analytical error for Precambrian samples.

Using the isotopic composition of air argon and measuring the  $\text{Ar}^{36}$  content, it has been found that the following approximate amounts of contaminant argon may be expected for the common K-Ar minerals:

Biotite:	$1-5 \times 10^{-6}$ cc. STP $\text{Ar}^{40}$ /gm
Hornblende:	$1-2 \times 10^{-6}$ "
Muscovite:	$0.5-2 \times 10^{-6}$ "
Sanidine:	$1-5 \times 10^{-7}$ "

These orders-of-magnitude of contamination are found irrespective of the age of the mineral, and vary with the geochemical setting. The relative importance of the daughter contaminant decreases with increasing age of the sample, and very young samples are thus relatively highly contaminated. The blank on the vacuum-extraction train may also become critical in the determination of Pleistocene dates. It is usually not too difficult to keep the blank below the order of  $10^{-7}$  cc. STP  $\text{Ar}^{40}$ , if this is necessary. Pyroxenes may show an excess of  $\text{Ar}^{40}$  (HART and DODD, 1961).

#### 4. Gain or Loss of Parent or Daughter

In order to evaluate this factor one must obtain comparative data. Cogenetic minerals have been dated, K-Ar has been compared with other "clocks", and out of a large amount of data some definite facts have been obtained. As one might expect, the loss of the daughter  $\text{Ar}^{40}$  plays by far the major role in the resetting of the K-Ar "clock". Certain minerals have been found to lose at least a portion of their  $\text{Ar}^{40}$  very easily. Among these are orthoclase, microcline, plagioclase, sylvite, clay minerals, glauconite and devitrified glass. Because of apparent argon loss, these minerals are largely unsuitable for dating by K-Ar. The following minerals have been shown to be more generally useful in this regard: Micas, hornblende, sanidine, high temperature low-K-feldspars and pyroxene. Any mineral, of course, may be altered or recrystallized by metamorphism, and so all of the minerals are susceptible to loss of  $\text{Ar}^{40}$ . Since  $\text{Ar}^{40}$  can escape relatively easily from biotite undergoing thermal metamorphism, the biotite K-Ar date is often used as the indicator of the latest thermal event in an area.

In general, the ease of response of K-Ar ratio in mafic minerals to thermal metamorphism is in the same mineral order as Bowen's reaction series. The sedimentary minerals are the most easily affected as regards Ar-loss, and low temperature dynamic metamorphism apparently will extensively reset the K-Ar "clock" in clay minerals and even micas. Samples from the same formation in which the grade of metamorphism ranged from slate to coarse gneiss yielded essentially the same K-Ar dates in a study in the Pe of Minnesota (GOLDICH et al., 1961). Thermal metamorphism without dynamic effects is also effective in resetting the K-Ar "clock" (HART, 1963).

### 5. Sampling

The wide distribution and high crustal abundance of potassium makes possible use of the K-Ar "clock" very extensive. A few grams of material are all that is necessary, but care should be taken to insure essentially monomineralic samples because of variable  $\text{Ar}^{40}$  loss. Except for sanidine and "sanidine-like" low K-feldspars, the feldspars are best avoided for K-Ar dating. Microcline, for example, apparently allows the formation of a fraction of its  $\text{Ar}^{40}$  in a lattice position from which it is very easily lost. Weathered materials should be avoided, if at all possible, since they are difficult to purify and often contain reduced amounts of parent and daughter. Since the latest thermal event is obtained with K-Ar dating, one usually will not be able to distinguish a sequence of older events in a more recently metamorphosed area. Unaltered primary intrusives and flat-lying unmetamorphosed bentonite beds yield K-Ar dates which are very close to the time of intrusion or laying down of the ash bed.

## III. $\text{Rb}^{87}$ - $\text{Sr}^{87}$

### A. General Description

$\text{Rb}^{87}$  emits  $\beta$ -particles of widely varying energies and is thus transformed into  $\text{Sr}^{87}$ . Having an alkali element parent, the Rb-Sr "clock" is in principle applicable to the same minerals as K-Ar, but is limited somewhat by two main factors. First,  $\text{Rb}^{87}$  has a longer half-life than  $\text{K}^{40}$  ( $\sim 50 \times 10^9$  years), and second, relatively large amounts of contaminant Sr are present in many Rb-bearing minerals. Unlike  $\text{Ar}^{40}$ , the chemical bonding of Sr makes its presence possible even in minerals where there may be relatively little Ar contamination. Nevertheless, the Rb-Sr "clock" may be used together with K-Ar in a wide variety of situations, especially in Precambrian rocks.

### B. Analytical Measurements

Except for certain Rb-rich minerals such as amazonite, lepidolite and pollucite, Rb is generally present in an amount ranging from 10-500 p.p.m. in suitable minerals. Isotope dilution is used to determine the amount of Rb, which has the isotopic composition (NIER, 1950):

$$\begin{aligned} \text{Rb}^{87} &- 27.85 \text{ atomic per cent} \\ \text{Rb}^{85} &- 72.15 \text{ atomic per cent.} \end{aligned}$$

Essentially pure  $\text{Rb}^{87}$  is added to the sample in an amount approximately one-half to double the estimated amount of  $\text{Rb}^{85}$ . Following chemical separation of the Rb, usually by ion exchange techniques, the  $\text{Rb}^{85}/\text{Rb}^{87}$  ratio is measured on a solid source mass spectrometer. The abundance of  $\text{Rb}^{87}$  in normal Rb is used to calculate the  $\text{Rb}^{87}$  content of the sample since  $\text{Rb}^{87}$  is used as the "spike" isotope. A variety of other methods may be used to determine total Rb (and thus  $\text{Rb}^{87}$ ). Among these are X-ray fluorescence, flame photometry, and spectrographic procedures.

Sr<sup>87</sup> is generally determined by isotope dilution since the isotopic composition of the extracted Sr must be assessed. If the amount of radiogenic Sr<sup>87</sup> in the sample is large, enriched Sr<sup>86</sup> may be used as the isotopic dilutant or "spike". To obtain the amount of Sr<sup>87</sup>-contaminant (or normal-Sr<sup>87</sup>) the Sr<sup>88</sup>/Sr<sup>86</sup> is measured, and the amount of normal Sr computed. Providing the normal-Sr<sup>87</sup> correction is not too large, the isotope abundance ratios for the normal-Sr may be taken to be that given by BAINBRIDGE and NIER (1950):

Sr<sup>84</sup> - 0.56 atomic per cent  
Sr<sup>86</sup> - 9.86 atomic per cent  
Sr<sup>87</sup> - 7.02 atomic per cent  
Sr<sup>88</sup> - 82.56 atomic per cent

In the event Sr<sup>87</sup> contaminant is very large, it is more advisable to utilize an isochron plot analysis to determine the date (Fig. 3).

### C. Evaluation

#### 1. Decay constants

Because of the low decay rate and large proportion of low-energy  $\beta$ -particles in the radiation spectrum of Rb<sup>87</sup>, accurate determination of the decay constant of Rb<sup>87</sup> is difficult. Recent results utilizing solid phosphors and scintillation counting have given results of from  $\lambda = 1.18 \times 10^{-11}$ /years to  $\lambda = 1.6 \times 10^{-11}$ /years (9, 10, 11). FLYNN and GLENDENIN (1959) obtained  $\lambda = 1.47 \pm 0.03 \times 10^{-11}$ /years by liquid scintillation counting while ALDRICH, et al. (1956) determined a value of  $\lambda = 1.39 \times 10^{-11}$ /years by comparing Sr<sup>87</sup>/Rb<sup>87</sup> ratios with concordant U-Pb dates given by cogenetic uranium minerals from the same rocks. The latter two values are most in favour at the present time, and the six per cent difference between them will soon be larger than the precision of the statistical mean for comparative results with the other nuclear clocks. Perhaps a choice will be possible between these two values in the near future.

#### 2. Analytical Sensitivity

Down to 0.1  $\mu$ g Rb and 1  $\mu$ g Sr may be isotopically analyzed on a suitable solid source mass spectrometer. Unless one takes special precautions, ordinary blanks (0.2 - 1.0  $\mu$ g Rb and 0.1 - 0.3  $\mu$ g Sr) determine the limiting level of precise isotopic measurement. Interlaboratory checks indicate that a precision of the order of 2-3 per cent can be expected in the determination of Sr<sup>87</sup>\*/Rb<sup>87</sup> for a Precambrian biotite. In isochron-plotting or when the amount of contaminant daughter is high, the Sr<sup>87</sup>/Sr<sup>86</sup> ratio of the sample must be determined as accurately as possible. This value may be measured now to a precision within one part per thousand with careful work.

#### 3. Contaminant Daughter

The amount of normal strontium in various Rb-containing minerals varies widely. Unfortunately, the most widespread available mineral for Rb-Sr, potassium feldspar, often contains relatively large amounts of normal strontium.

Table II  
Possible proportion of  $\text{Sr}^{87*}$  to total  $\text{Sr}^{87}$  in various minerals  
taken to be 1175 m.y. old

Mineral	Rb, p.p.m.	Normal $\text{Sr}(\text{Sr}^{\text{N}})$ , p.p.m.	$\text{Sr}^{87*}$ , p.p.m.	$\text{Sr}^{87*}$ in total $\text{Sr}^{87}$ , per cent
Pegmatitic Biotite	1926	3.5	9.7	97.5
Pegmatitic Muscovite	3970	2	20	99.3
Pegmatitic Lepidolite	25000	1	126	99.94
Pegmatitic K-feldspar	552	17.0	2.78	70.2
Gr. Gneiss K-feldspar	552	350	2.78	10.2

Table III

Error in  $\text{Sr}^{87*}$  due to a one per cent error in  $\text{Sr}^{87\text{N}}$  determination for mica of different ages containing 1 p.p.m.  $\text{Sr}^{87\text{N}}$  and 250 p.p.m.  $\text{Rb}^{87}$

Age, m.y.	$\text{Sr}^{87*}$ , p.p.m.	$\frac{\text{Sr}^{87*}}{\text{total Sr}^{87}} \times 100$	Percentage error in $\text{Sr}^{87*}$ from a one per cent error in the $\text{Sr}^{87\text{N}}$ -determination
2670	10.2	91	0.1
680	2.5	71	0.4
68	0.25	20	4
6.8	0.025	2.4	40

The larger amounts of radiogenic strontium ( $\text{Sr}^{87*}$ ) in Precambrian samples often makes the normal strontium content tolerable, but relatively few Paleozoic feldspars (except pegmatitic) have a low enough normal Sr-content to permit reasonably accurate Rb-Sr dating. An example of the variation of normal Sr in several minerals and the relative effect on the percentage of radiogenic  $\text{Sr}^{87}$  in these minerals is given in Table II. The minerals are all given the same date, 1175 m.y., but the younger the minerals become, the less the proportions of  $\text{Sr}^{87*}$  to contaminant  $\text{Sr}^{87}$ . To assess this factor, the age of a mica containing relatively little normal  $\text{Sr}^{87}$  ( $\text{Sr}^{87\text{N}}$ ) may be varied and the effect of an error in the  $\text{Sr}^{87\text{N}}$ -determination examined. In Table III one can readily see that the younger the sample is, the greater the error introduced by the error in  $\text{Sr}^{87\text{N}}$ -correction. Given a one per cent error in the  $\text{Sr}^{87\text{N}}$  determination, the critical quantity to note is the proportion of radiogenic  $\text{Sr}^{87}$ . Lepidolite is suitable even for Tertiary samples, while K-feldspar is usually suitable only for Precambrian samples unless it is unusually Rb-rich (amazonite) or Sr-poor (pegmatitic).

#### 4. Gain or loss of Parent or Daughter

One might expect  $\text{Sr}^{87*}$  to be retained more readily than the inert gas  $\text{Ar}^{40}$ , but this is not necessarily the case. When the host mineral is not a good locus for Sr, such as in the case of micas, the partial molal free energy of Sr in the

mineral is generally much higher than in the surrounding matrix, and the tendency for Sr to leave the mica lattice is high. It has been found that in thermal metamorphism (GAST and HANSON, 1962; HART, 1963) Sr is lost with about the same ease as Ar<sup>40</sup> in micas. K-feldspar retains Sr better than phyllosilicates since Sr can substitute diadochically for K. There is some evidence that K-feldspar may even take up Sr<sup>87\*</sup> in certain cases, but, by and large, recrystallization resets the Rb-Sr clock in K-feldspar. The Sr<sup>87\*</sup> which leaves the Rb-bearing minerals during metamorphism is taken up by newly-formed Sr-bearing metamorphic minerals or by recrystallizing minerals such as apatite and plagioclase.

Since most Sr<sup>87\*</sup>-rearrangement during metamorphism is apparently a short-range process, graphical analysis of the variation of Sr<sup>87\*</sup>-content with time can aid in establishing the time of metamorphism (COMPSTON and JEFFERY, 1961).

Let the subscript 0 denote the time at which a rock or mineral first became a closed system and p denote the present time. Combining the known relations

$$Rb_0^{87} = Rb_p^{87}e^{\lambda t}$$

and

$$\begin{aligned} Rb_0^{87} - Rb_p^{87} &= Sr_p^{87*} \text{ (radiogenic only),} \\ Rb_p^{87}(e^{\lambda t} - 1) &= Sr_p^{87*} \end{aligned} \quad (1)$$

is obtained. Considering the change in the total amount of Sr<sup>87</sup>,

$$Sr_p^{87} = Sr_0^{87} + Sr_p^{87*}$$

substituting (1),

$$Sr_p^{87} = Sr_0^{87} + Rb_p^{87}(e^{\lambda t} - 1). \quad (2)$$

Using the approximation  $(e^{\lambda t} - 1) \cong \lambda t$  and dividing through by Sr<sup>86</sup> (invariant), (2) becomes

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p \cong \left(\frac{Sr^{87}}{Sr^{86}}\right)_o + \left(\frac{Rb^{87}}{Sr^{86}}\right)_p \lambda t \quad (3)$$

solving for t,

$$t \cong \frac{Sr^{86}\lambda}{Rb^{87}} \left[ \left(\frac{Sr^{87}}{Sr^{86}}\right)_p - \left(\frac{Sr^{87}}{Sr^{86}}\right)_o \right]. \quad (4)$$

This is the equation of a straight line with a slope of Sr<sup>86</sup>λ/Rb<sup>87</sup>, if we plot t vs. (Sr<sup>87</sup>/Sr<sup>86</sup>). Figure 2 represents such a plot for a granite which has remained a closed system since emplacement despite a strong metamorphic event at t = t<sub>m</sub>. The normal and radiogenic strontium is assumed to have been thoroughly mixed at the time of metamorphism through recrystallization of the minerals or by free solid-state diffusion. The period of metamorphism is short compared with the periods of time before and after the metamorphism.

Starting with an initial Sr<sup>87</sup>/Sr<sup>86</sup> = 0.71 for the rock and its minerals, the change in Sr<sup>87</sup>/Sr<sup>86</sup> with time is seen (Fig. 2) to increase in proportion to the Rb-content of the phase (since λ and Sr<sup>86</sup> are constant). When the rock is metamorphosed at time t<sub>m</sub>, the Sr in the rock is redistributed (and "homogenized") according to the partial molal free energy of Sr in the various minerals. The Rb/Sr in the recrystallized minerals need not be the same as

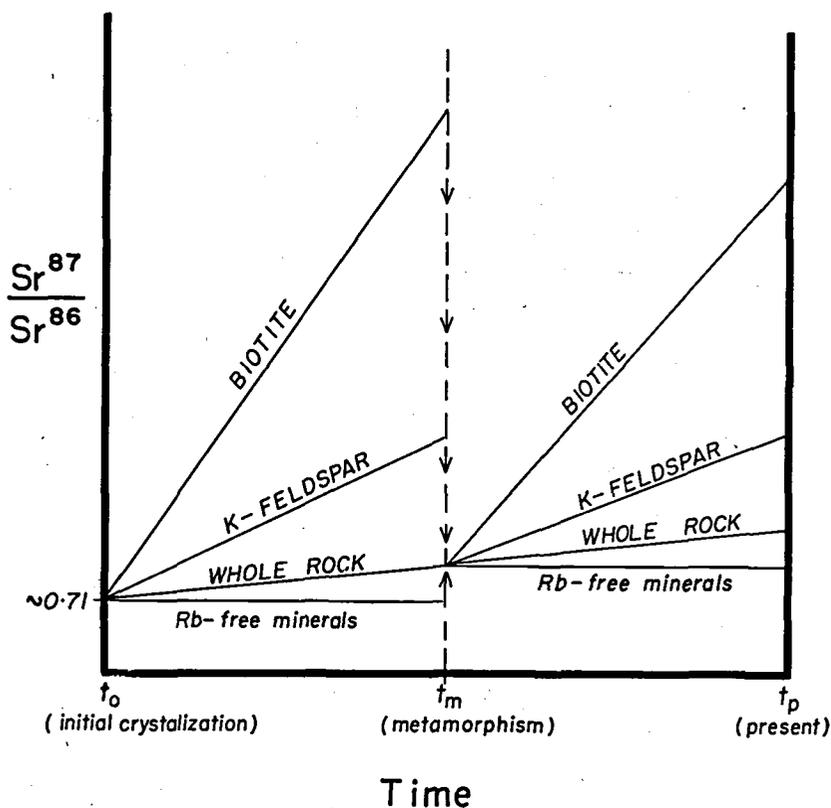


Figure 2. Effect of metamorphism (short-range diffusion and recrystallization) on the change in  $\text{Sr}^{87}/\text{Sr}^{86}$  with time in a rock (closed system) and its constituent minerals (open systems).

formerly and so the slopes of the growth lines may be different after metamorphism. The whole rock growth line is unaffected, because of the postulate that the rock is a closed system. The  $\text{Sr}^{87}/\text{Sr}^{86}$  in the recrystallized (or newly-formed) minerals grows again from the  $\text{Sr}^{87}/\text{Sr}^{86}$  value for the whole rock at  $t_m$ . From measurements of  $\text{Sr}^{87}/\text{Sr}^{86}$ , Sr-content and Rb-content of the rock and minerals at the present time, one may compute the slope of the growth line for each phase. The pattern of intersection of the plotted growth lines may then be interpreted. The time of metamorphism is found by the intersection of the growth lines of the recrystallized minerals and the whole rock, but the time of original emplacement,  $t_0$ , can be found only if  $(\text{Sr}^{87}/\text{Sr}^{86})_0$  is known. This may be determined by analysis of phases of the same rock of varying Rb/Sr (see Fig. 3).

If an emplaced rock (for example, a single intrusive of variable composition) contains a relatively high proportion of common strontium or if it is desired

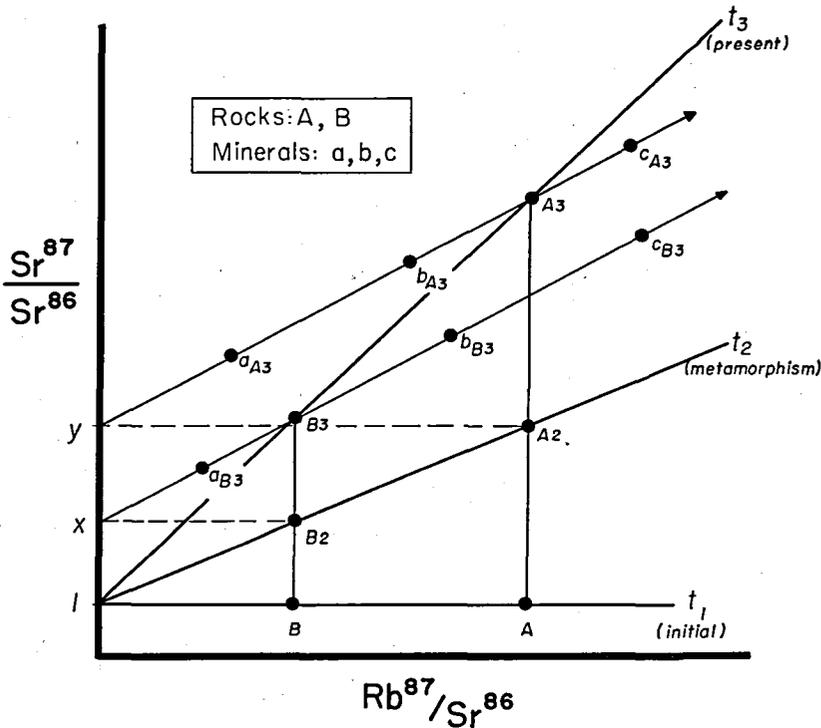


Figure 3. Variation in  $Sr^{87}/Sr^{86}$  vs.  $Rb^{87}/Sr^{86}$  for two whole rock phases (A and B) of a intrusive, and the effect on constituent minerals by a metamorphic event at time,  $t_2$ .

to find a real or precise value for  $(Sr^{87}/Sr^{86})_0$  for the rock, the so-called "isochron" plot of

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p \cong \left(\frac{Sr^{87}}{Sr^{86}}\right)_0 + \frac{Rb^{87}}{Sr^{86}} \lambda t \quad (3)$$

may be used.  $Rb^{87}/Sr^{86}$  is plotted versus  $Sr^{87}/Sr^{86}$  to give a straight line of slope  $\lambda t$  which intersects the  $(Sr^{87}/Sr^{86})$  axis at  $(Sr^{87}/Sr^{86})_0$ . Consider the plot in Fig 3. At  $t_1$ , when  $Sr^{87}/Sr^{86} = 1$ , the phases A and B of an intrusive rock crystallize and form closed systems. If A and B are closed systems, even during metamorphism, then at the present time,  $t_3$ , the plot still gives the  $(Sr^{87}/Sr^{86})_0 = 1$ . If a metamorphic event at time,  $t_2$ , thoroughly remixes the Sr within the rock, then the Rb-bearing minerals within phase B will begin accumulating  $Sr^{87}$  from  $(Sr^{87}/Sr^{86}) = x$  and the minerals in phase A from  $(Sr^{87}/Sr^{86}) = y$ . At time,  $t_3$ , the  $Sr^{87}/Sr^{86}$  values for the minerals in phase B will lie along the line  $x B_3$  and in phase A along the line  $y A_3$ . Since the slope of either  $x B_3$  or  $y A_3$  gives the time (ago) of the metamorphism, they must be parallel. Deviations from this pattern indicate violation of the basic assumptions, especially likely with regard to thorough remixing of the Sr.

IV.  $U^{238} - Pb^{206}$ ,  $U^{235} - Pb^{207}$ ,  $Th^{232} - Pb^{208}$ ,  $Pb^{207} - Pb^{206}$ 

## A. General Description

These parent-daughter pairs will be considered together since all of them may be applied simultaneously to most older U-Th minerals.  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  all are the long-lived progenitors of a series of consecutive radioactive nuclides. This consecutive series ends with the formation of a stable lead isotope in each case. Table IV gives the stable decay products and the constants for the three parents.

Table IV  
Decay constants for  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$

Nuclide	Stable Decay Products	$\lambda$ , yr. <sup>-1</sup>	Half life, yrs.
$U^{238}$	$Pb^{206} + 8He^4$	$1.54 \times 10^{-11}$	$4.51 \pm 0.02 \times 10^9$
$U^{235}$	$Pb^{207} + 7He^4$	$9.72 \times 10^{-10}$	$7.13 \pm 0.16 \times 10^8$
$Th^{232}$	$Pb^{208} + 6He^4$	$4.99 \times 10^{-11}$	$1.39 \pm 0.03 \times 10^{10}$
			(KOVARIK and ADAMS, 1955)
			(FLEMING et al., 1952)
			(KOVARIK and ADAMS, 1938)

The ratio  $Pb^{207}/Pb^{206}$  (radiogenic) may be used to calculate a fourth date for a U-Th mineral since the decay rates of  $U^{238}$  and  $U^{235}$  are different, and the ratio thus varies with time. Such a date is not an independent number, but has special significance in the case where there is lead loss from the mineral after first closure of the system. When all four possible dates from a U-Th mineral are determined, it may be seen from the similarity or concordance of the dates whether or not a possible disturbance of the initially-closed mineral system has taken place. This "concordance test" is of great value in interpreting the meaning of the data obtained as well as evaluating the reliability of various minerals for U-Th-Pb dating.

## B. Analytical Measurements

Isotope dilution is used most often for the accurate determination of small amounts of U and Th (as in zircon).  $U^{235}$  and  $Th^{230}$  are utilized as isotope dilutants or spikes, and  $U^{235}$  in a sample is computed from the known ratio of  $U^{238}/U^{235}$  in natural uranium (139.6, weight ratio) and the determined amount of  $U^{238}$ . Total uranium may be determined by a number of methods, which include fluorescence photometry, colorimetry, polarography and  $\alpha$ -counting for small amounts; while classical gravimetric and titrimetric procedures may be used for samples high in uranium. Thorium may be determined by colorimetry for small amounts or by titrimetric and gravimetric procedures for large amounts. Since  $U^{238}$  and  $U^{235}$  together account for essentially 100 per cent of natural uranium and since the abundance of  $Th^{232}$  in thorium is also essentially

100 per cent,  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  may be easily obtained from determinations of total U and total Th.

If Pb is present in large amounts, conventional chemical methods may be used in quantitative determination. For small amounts ( $< 1000$  p.p.m.), colorimetry and isotope dilution are used. Samples rich in  $Pb^{208}$  (high U, low Th) are "spiked" with  $Pb^{208}$ , and samples rich in  $Pb^{208}$  (low U, high Th) are "spiked" with  $Pb^{206}$ . An isotopic analysis of the unspiked lead must be made, and therefore isotope dilution is often used for the quantitative determination of the Pb.

Blanks on chemical extraction procedures for subsequent isotope dilution determinations of U and Th yield negligible contamination for minerals amenable to dating. Pb separation from low-Pb minerals such as zircon may involve fluxing, double dithizone extraction and PbS precipitation, in which case as much as one to five per cent of the final, spiked PbS precipitate (weighing 10–50  $\mu$ g.) may be laboratory Pb contaminant – mainly from the Pb in the air. Since the sensitivity of the mass spectrometric determination of Pb is very high, both the amount and isotopic composition of this blank may be precisely determined and applied as a correction in a standard procedure. Samples high in radiogenic lead and susceptible to simple acid dissolution, such as uraninite, may have a negligible blank correction. Vacuum evaporation of Pb and conversion to lead tetramethyl yields lower blanks than chemical extraction methods.

### C. Evaluation

#### 1. Decay Constants

The decay constants for  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  have been measured with good accuracy (see Table IV). A discussion of the various measurements has been presented in a review by ALDRICH and WETHERILL (1958). In general, the precision of measurement of the decay constants for  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  is much better than that for  $K^{40}$  or  $Rb^{87}$ ; being better than one per cent for  $U^{238}$  and about two per cent for  $U^{235}$  and  $Th^{232}$ .

#### 2. Analytical Measurements

The mass spectrometric methods of isotope dilution make possible the determination of very small amounts of U, Th and Pb. Down to 0.1 p.p.m. U, 1 p.p.m. Th and 0.01 p.p.m. Pb may be precisely determined. As with the preceding "nuclear clocks", the real limitations on the precise measurement of the radiogenic lead are set by the degree of blank Pb and the amount of common Pb contaminant in the samples. The common Pb contaminant is estimated from the  $Pb^{204}$  after correcting for the blank, and the smaller  $Pb^{204}$  peak must be carefully measured.

#### 3. Contaminant Daughter

The amount of contaminant, non-radiogenic lead in a mineral will vary according to how well Pb is accepted in the mineral lattice. For example,

sphene and apatite, while they possess suitable amounts of U and Th, generally contain such a high proportion of non-radiogenic Pb that determination of the radiogenic Pb isotopes is very difficult. On the other hand, zircon and especially uraninite tend to contain relatively little non-radiogenic lead compared with radiogenic lead. A correction for relatively small amounts of non-radiogenic lead ( $< 10\%$ ) may be made since normal or common Pb contains  $Pb^{204}$ , an isotope not formed via any known natural process of radioactive decay. If one envisions common lead as coming from a continuously-mixed deep (mantle?) source of low U and Th content, the isotopic composition of this lead will change slowly with time. Such a change will be much less than that for a crustal mineral. The isotopic composition of this deep-seated common Pb will vary approximately between  $Pb^{204} : Pb^{206} : Pb^{207} : Pb^{208} = 1 : 12 : 14 : 32$  and  $1 : 19 : 16 : 39$  from  $\sim 3000$  m.y. ago to the present (see RUSSELL and FARQUHAR, 1960). If the history of the common lead contaminant involves mixing of the deep-seated Pb with crustal radiogenic Pb before incorporation in a mineral, the exact isotopic composition of the contaminant Pb will be very difficult to specify. Thus, it is readily seen that the relative amount of contaminant Pb must be small if the error made in judging its isotopic composition is not to cause too large an uncertainty in the determination of the radiogenic isotopes. If it is possible to find contaminant Pb in a U-Th-free cogenetic mineral, then the isotopic composition of this Pb may be used for that of the contaminant Pb. For example, the isotopic composition of Pb in K-feldspar or galena formed at the same time as coexisting zircon should be essentially the same as that Pb initially incorporated in the zircon.

In uranium-bearing minerals the corrections for contaminant daughter lead affect the precision of the  $Pb^{206}$ -determination the least, the  $Pb^{207}$ -determination about ten times as severely and the  $Pb^{208}$ -determination from five to fifty times as severely, depending on the Th-content of the mineral. If Th is very high, the  $Pb^{208}$ -content may be so high that the contaminant correction is almost negligible. Most of the contaminant Pb correction error in the  $Pb^{207}/Pb^{206}$  date comes from the error in correcting  $Pb^{207}$ .

#### 4. Gain or loss of Parent or Daughter

It was recognized early in U-Pb dating attempts that the relative ratios of

Table V  
Concordant and discordant U-Pb dates

Sample	$U^{238}/Pb^{206}$ m.y.	$U^{235}/Pb^{207}$ m.y.	$Pb^{207}/Pb^{206}$ m.y.	$Pb^{208}/Th^{232}$ m.y.
Ceylon gem zircon (TILTON et al., 1957)	$540 \pm 12$	$544 \pm 16$	$555 \pm 30$	$538 \pm 25$
Zircon, massive granite N. E. Alberta	1390	1580	1850	1530
Monazite, mineralized biotite schist, N. E. Alberta	2290	2110	1945	1880

parent to daughter in U-Th-bearing minerals often are out of balance. This balance or concordance may be tested since there are up to four dates obtainable from a U-Th mineral. An example of concordant dates (Ceylon zircon) and the two most frequent patterns of discordant dates are given in Table V.

In searching for the causes of discordant U-Pb dates, it is found that the possibilities are somewhat more numerous than for K-Ar or Rb-Sr. The loss of intermediate products in each of the long decay series must be considered along with the parent and daughter. Because of the very small amount of each of the intermediate members in the radioactive series, only the loss of the rare gas Rn is considered in Fig. 4.

It is seen from Fig. 4 that the two patterns of discordance in Table V are accounted for by loss of Pb (or gain of U) and loss of U (or gain of Pb). Rn-loss has been observed in the laboratory from the amorphous, poorly-crystallized U-minerals, but for zircon and monazite this loss is likely not significant. Monazite often shows a U-loss discordance pattern, but usually shows Pb-loss discordance. Zircon almost always shows Pb-loss discordance. From a consideration of the discordance patterns, petrographic observations and the geochemistry of U and Pb, it appears that Pb-loss causes most discordant dates and apparent U-loss discordance occurs to a lesser extent in minerals such as monazite. Gain of Pb or U is a rarer cause of discordance.

WETHERILL (1956) showed that if loss of Pb occurs in a single episode (strong metamorphic event) after the original formation of the U-bearing mineral, then a "concordia" plot of  $Pb^{207}/U^{235}$  versus  $Pb^{206}/U^{238}$  for cogenetic samples of varying Pb-loss will yield a straight line. This straight line will be a chord of the concordia\*) arc which intersects the concordia at the time of original formation of the minerals and the time of the subsequent episodic lead loss. In certain disturbed areas, such a plot has given data which fits all

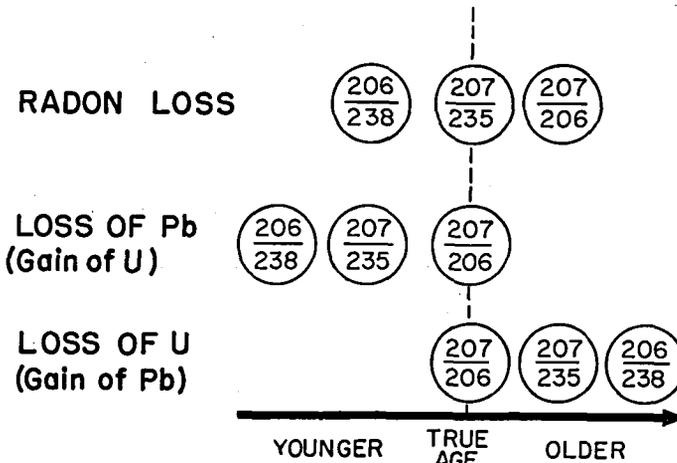


Figure 4. Effect of loss of Rn and gain or loss of U and Pb on the  $Pb^{207}/U^{235}$ ,  $Pb^{206}/U^{238}$  and  $Pb^{207}/Pb^{206}$  dates.

\*) The concordia is the locus of points at which  $Pb^{206}/U^{238}$  and  $Pb^{207}/U^{235}$  give the same date.

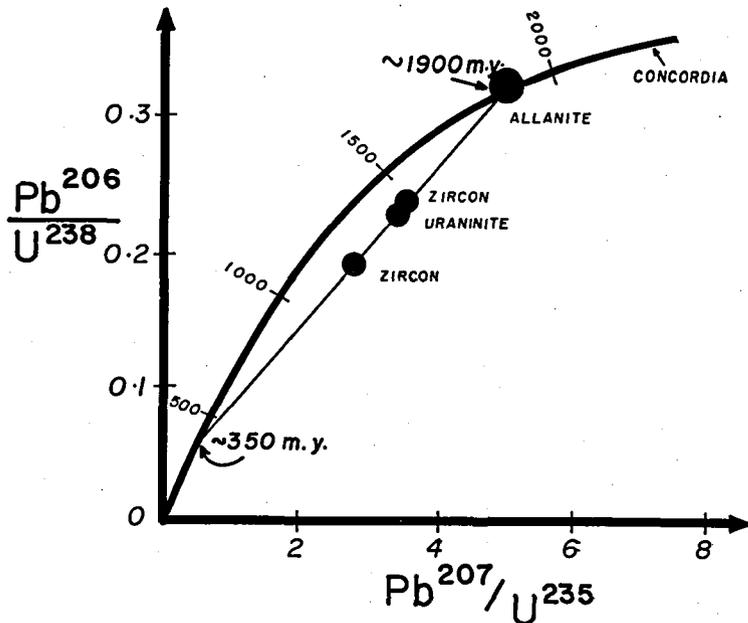


Figure 5. Concordia plot for mineral samples from the Canadian Shield of N. E. Alberta near Andrew Lake.

the geologic and accessory geochronologic data very well. In many other areas, however, a plot such as that in Fig. 5 is observed.

For the example in Fig. 5, an episodic lead loss at  $\sim 350$  m.y. ago is very unlikely since there is no indication that the area has been disturbed seriously since 1800 m.y. ago. In such cases, another mode of lead loss must be sought. TILTON (1960) showed that if samples from different continents whose 207/206 date is  $> 2300$  m.y. are plotted on a concordia diagram, a chord is obtained which yields  $T_1 = 2800$  m.y. and  $T_2 = 500-600$  m.y. The samples chosen were from different continents and for many there is no indication of a secondary event in the area of collection. Tilton concluded that a general mechanism of Pb-loss must be responsible for much of the discordancy. He then proposed that Pb may diffuse slowly from the mineral over its lifetime, rather than being lost at one or more discrete intervals. A plot of this model of Pb-loss on a concordia diagram gives a straight line over most of the concordia plot, but the line curves to the origin at the low values of 206/238 and 207/235. No secondary event is invoked and such a plot explains the distribution of discordant lead dates which Tilton compiled for the various continents. Tilton also recognized that there is a possibility for both episodic and diffusion-loss of Pb for a single group of U-minerals. Fig. 6 shows the relationships expected for the rapid episodic loss of Pb 1800 m.y. ago superimposed on Pb-loss by diffusion from 2800 m.y. old minerals. The limiting cases in this situation are given by the lines labelled "diffusion (1)", "diffusion (2)" and

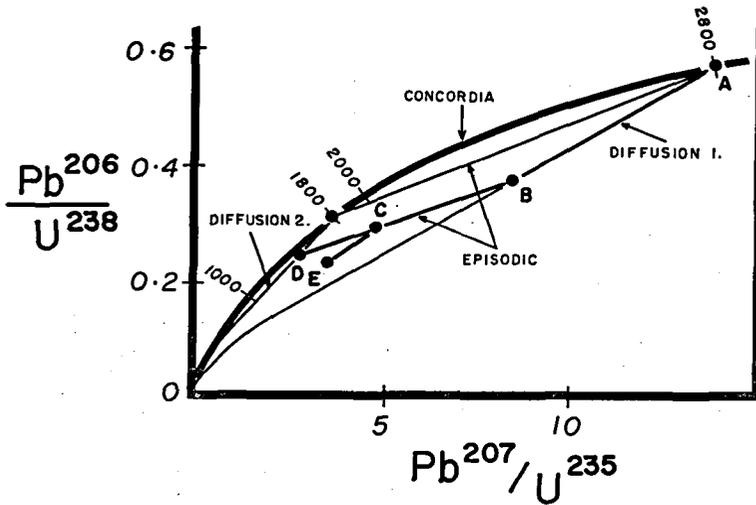


Figure 6. Parent-daughter ratios resulting from the episodic loss of Pb 1800 m.y. ago superimposed on continuous loss of Pb by diffusion for 2800 m.y. old minerals.

“episodic”. The variation in 206/238 vs. 207/235 might vary as follows. Starting at A, the mineral loses Pb by diffusion and at 1800 m.y. ago the lead plots at B. Undergoing episodic loss of Pb the composition of the Pb shifts along line BD (line of equal  $D/a^2$ ) but due to incomplete loss of Pb stops at C.

From point C, the mineral loses Pb by diffusion (again at same  $D/a^2$ ) up to the present time, when its composition may plot at about point E. It can be seen that a combination of diffusion and episodic loss may make the final composition of the Pb plot almost anywhere within the three boundary lines. A mixture of 1800 m.y. and 2800 m.y. zircons undergoing diffusion loss of lead will also plot within the roughly triangular field in Fig. 6 and cannot be distinguished from a combined episodic-diffusion Pb loss history for a single mineral without other information. In practice it has been found that most groups of zircons from cogenetic rock phases plot on some sort of straight line relationship on a concordia diagram. TILTON (1960) has estimated activation energies of the order of 3–10 Kcal/mole for diffusion of Pb in the temperature range 50–600°C. Since diffusion of Ar from biotite involves activation energies of the order of 5–10 times as large, one must account for this surprisingly low activation energy for Pb-loss. Measurements by SILVER (1962) have shown that the more radioactive a zircon sample from a single zircon population, the more discordant the dates. In addition, sample radio-activity increased with decreasing grain size and increasing magnetic susceptibility. The more radioactive bombardment a crystal lattice such as zircon has to absorb, the more metamict it becomes. It may be argued that the damaged zircon lattice gives up Pb much more readily than an undamaged lattice, and that time-controlled lattice damage gives rise to some sort of time-controlled Pb loss. At any rate, concordia plotting of populations of U-bearing minerals almost always gives a reasonably regular relationship which may be utilized in interpreting the data. The interpretations

thus obtained rest upon knowledge of the causes of discordance in U-minerals and are still incompletely explained.

Other data bears on the problem of discordancy in U-Pb dates. TILTON (1956) performed acid-washing experiments to determine the effect of leaching on various minerals. Essentially, he found that specimens which gave low  $\text{Th}^{232}/\text{Pb}^{208}$  dates vs. U/Pb dates yielded relatively high amounts of  $\text{Pb}^{208}$  when leached. In the case of some high  $\text{U}^{238}/\text{Pb}^{206}$  dates, more  $\text{Pb}^{206}$  than  $\text{Pb}^{208}$  was leached out. The excess  $\text{Pb}^{208}$  was accompanied by excess  $\text{Th}^{232}$  while in the case of excess  $\text{Pb}^{206}$ , excess  $\text{U}^{238}$  accompanied the  $\text{Pb}^{206}$  into the leach. TILTON (1956) concluded that the amount of loss of various Pb isotopes in acid leaching of a mineral is not necessarily proportional to their abundances in a given sample at present. That the Th or U, and thus the daughter, were in special, easily-reached lattices positions is evident, but the question of exactly how and why these positions came about is still unsolved. That the leaching is related to damage or alternation of the crystal is likely. Concordant minerals tested gave little loss and negligible distortion of isotope patterns, while highly discordant altered or metamict minerals generally reacted to leaching in a manner related to their discordancy.

Other workers have suggested that radioactive equilibrium between the intermediate members of the U and Th series may be disturbed. This points to an effect involving intermediates, possibly combined with recoil effects and lattice damage. The different energies of various daughters between the  $\text{U}^{238}$  and  $\text{U}^{235}$  series could accentuate discordancy.

## 5. Sampling

Samples for U-Pb dating generally need to contain U, Th or both in amounts such that at least 5–10 ppm of radiogenic Pb has been generated. In addition, the mineral or rock chosen must contain relatively little ordinary or non-radiogenic lead. Minerals that have been used include:

Uraninite (Thucolite, pitchblende, microlite)	$\text{UO}_2$
Thorite	$\text{ThSiO}_4$
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 8\text{H}_2\text{O}$
Monazite	$\text{CePO}_4 + \text{La-rare earths} + \text{Th}$
Allanite	$(\text{Ca, Mn, Ce, La, Y, Th})_2(\text{Fe}^{+2}, \text{Fe}^{+3}, \text{Ti})$ $(\text{Al, Fe}^{+3})_2\text{O} \cdot \text{OH}[\text{Si}_2\text{O}_7] [\text{SiO}_4]$ (Thorian epidote)
Columbite-Tantalite	$(\text{Fe, Mn})(\text{Ta, Nb})_2\text{O}_6$
Zircon	$\text{ZrSiO}_4$
Xenotime	$\text{YPO}_4$
Sphene	$\text{CaTi}[\text{SiO}_4](\text{O, OH, F})$
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH, F, Cl})$ .

The only usable mineral that is really widely distributed and most often present in the acidic rocks of the crust is zircon. Other minerals are relatively rare and occur in complex pegmatites or in mineral veins and mineralized rocks. Sphene and apatite have too high an affinity for common lead to be generally useful in U-Pb work. Pegmatitic uraninite is one of the best materials, when available.

### V. Dating Lead minerals by means of their isotopic constitutions

The major lead mineral considered is generally galena, but Pb held in the lattices of other primary sulfide minerals is also amenable to the following considerations. Unlike the U-Pb and Th-Pb dates determined on U-Th minerals, lead mineral or galena dates depend upon assumption of a definite model for the genesis of the lead mineral and for the change in isotopic composition with time. This model must be world wide if general applicability is to result, and must at least generally describe the formation of the U-free Pb minerals as well as the possible history of the Pb itself.

#### A. Theory and Models for Lead Mineralization

GERLING (1942), HOLMES (1946) and HOUTERMANS (1946) assumed that the ratios of  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  to  $Pb^{204}$  remained constant in locally closed systems from a time  $t_0$  when the earth formed, to a time  $t_1$  when mineralization isolated lead from the U and Th. The number of  $Pb^{206}$  atoms present at time  $t_1$  in any such closed system is

$$N_{t_1}^{Pb^{206}} = N_{t_0}^{Pb^{206}} + N_{t_0}^{U^{238}} - N_{t_1}^{U^{238}}$$

If we divide through by the number of  $Pb^{204}$  atoms, then, using the following symbols (RUSSEL & ALLAN (1956)):

Isotope ratio	at present time $t = 0$	at time $t = t$	at time $t = t_0$
$Pb^{206}/Pb^{204}$	a	x	$a_0$
$Pb^{207}/Pb^{204}$	b	y	$b_0$
$Pb^{208}/Pb^{204}$	c	z	$c_0$
$U^{235}/Pb^{204}$	V	$Ve^{\lambda't}$	$Ve^{\lambda't_0}$
$U^{238}/Pb^{204}$	137.8V	$137.8Ve^{\lambda t}$	$137.8Ve^{\lambda t_0}$
$Th^{232}/Pb^{204}$	W	$We^{\lambda''t}$	$We^{\lambda''t_0}$

Where:

$$\begin{aligned} \lambda' &= 0.9722 \times 10^{-9}/yr. && (U^{235}) \\ \lambda &= 0.1537 \times 10^{-9}/yr. && (U^{238}) \\ \lambda'' &= 0.0499 \times 10^{-9}/yr. && (Th^{232}) \end{aligned}$$

Then

$$x = a_0 + 137.8V (e^{\lambda t_0} - e^{\lambda t}).$$

Similarly for y and z:

$$\begin{aligned} y &= b_0 + V (e^{\lambda't_0} - e^{\lambda't_1}) \\ z &= c_0 + W (e^{\lambda''t_0} - e^{\lambda''t_1}). \end{aligned}$$

Eliminating V between the equations for x and y:

$$\emptyset = \frac{y - b_0}{x - a_0} = \frac{e^{\lambda't_0} - e^{\lambda't_1}}{137.8(e^{\lambda t_0} - e^{\lambda t_1})}$$

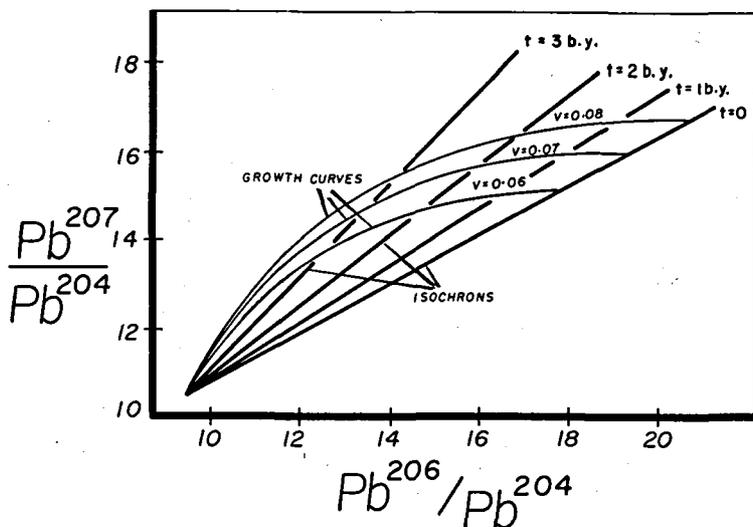


Figure 7. Growth curves and isochrons of the Holmes-Houtermans model (after RUSSEL & FARQUHAR (1960).

Since the right hand side of the equation is a constant for all leads mineralized at time  $t_1$ , all leads with age  $t_1$  will lie on a straight line in a plot of  $x$  vs.  $y$ . The relation is known as Houtermans' "isochron equation", since the lines of a given age are called isochrons (see Fig. 7).

The curved lines or growth curves are given for different values of  $V$ . Since  $V$  is eliminated in the isochron equation, only  $x$  and  $y$  need to be measured. The ages calculated using the equation are highly sensitive to the value of  $t_0$  chosen (as well as  $a_0$  and  $b_0$  to a lesser extent). Houtermans "calibrated" his equation by specifying  $x$  and  $y$  for a lead of zero age. More recently, PATTERSON (1955) found that meteoritic lead was the least radiogenic of any lead, and his lowest meteorite values are accepted today for  $a_0$  and  $b_0$ .

The excellent plot of  $207/204$  vs.  $206/204$  Pb in meteorites gives a precise value for the age of meteorites. Using diagonal linear regression through  $a_0 = 9.50$ ,  $b_0 = 10.36$  (average for Canon Diablo and Henbury),

Table VI  
Isotopic Composition of Pb in Meteorites (PATTERSON, 1956)

Meteorite	206/204	207/204	208/204
Nuevo Laredo, Mexico	50.28	34.86	67.97
Forest City, Iowa	19.27	15.95	39.05
Modoc, Kansas	19.48	15.76	38.21
Henbury, Australia	9.55	10.38	29.54
Canon Diablo, Arizona	9.46	10.34	29.44

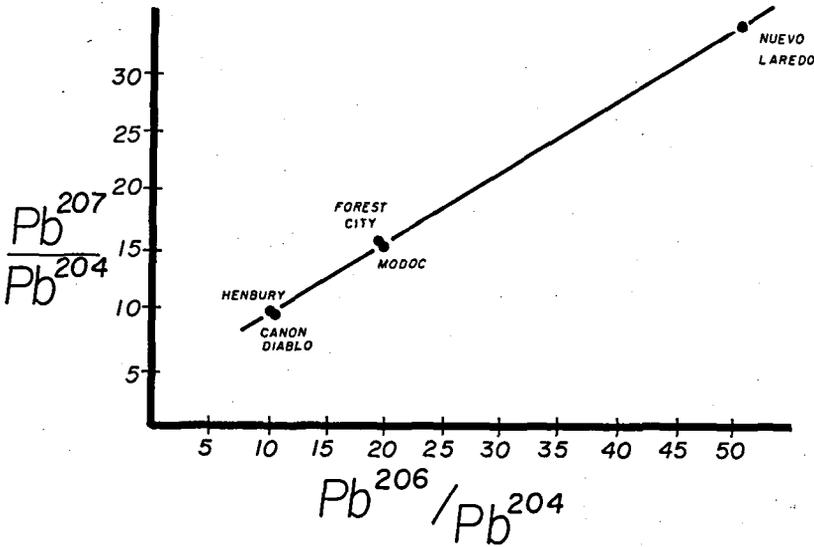


Figure 8. Lead extracted from Meteorites (PATTERSON, 1956).

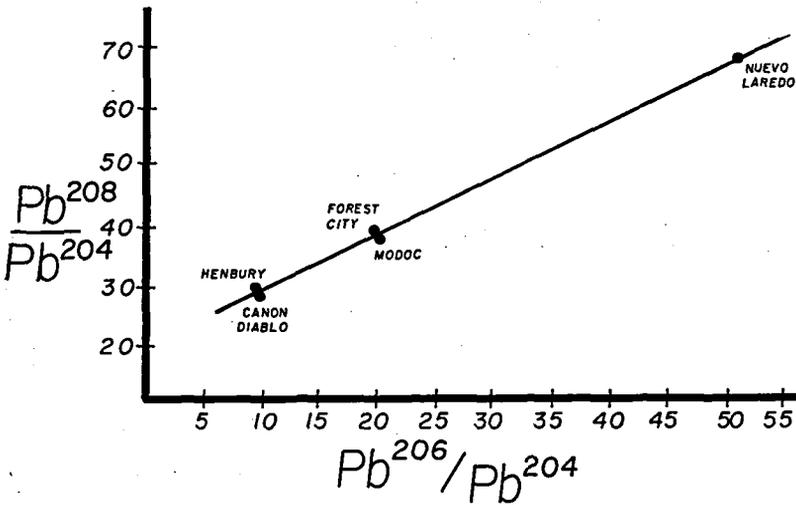


Figure 9. Lead extracted from meteorites (PATTERSON, 1956).

$t_0 = 4.56 \pm 0.02$  b.y. (KANASEWICH, 1962). Using  $208/204$ , a value of  $Th^{232}/U^{238} = 3.7$  can be determined. To tie in the meteoritic leads with terrestrial leads, CHOW and PATTERSON (1959, 1962) analyzed lead from manganese nodules and other ocean sediments. It is thought that the Pb in these samples represents a good average for modern terrestrial lead abundances. These leads fit the meteoritic plot reasonably well enough so that terrestrial leads and

meteoritic leads may be correlated. Thus the age of the earth is taken to be 4.56 b.y.

Returning briefly to Houtermans isochron equation, it may be evaluated and calibrated using Pattersons meteorite-derived  $a_0$ ,  $b_0$  and  $t_0$ .

RUSSELL (1956) (see also RUSSELL and FARQUHAR, 1960) has summarized the possible sequence of events in the lifetime of a Pb ore as follows:

- I. At the time of its formation, the earth contained in its mantle primeval lead disseminated with the uranium and thorium present.
- II. Lead in any part of the mantle was altered by the addition of the radiogenic isotopes Pb-206, Pb-207 and Pb-208 until the time of an orogenic event.
- III. At the time of the orogenic event, Pb was brought to the surface and was incorporated into crustal rocks.

Then follow six alternatives:

- IV. (a). The Pb remains indefinitely disseminated in the crustal rocks.
- IV. (b). The lead is incorporated directly into lead minerals, in which case it has a simple history and is what is called an ordinary lead.
- IV. (c). The Pb is incorporated into crustal rocks having uranium/lead and thorium/lead ratios similar to those in the mantle, and subsequently forms an ore mineral at a later time. Isotopically, this Pb is the same as Pb from the mantle at the time of mineralization.
- IV. (d). The Pb is incorporated into rocks having U/Pb and Th/Pb ratios much smaller than those in the mantle, and subsequent to the orogeny forms a Pb mineral. Isotopically the Pb is indistinguishable from that in case IV(b).
- IV. (e). The Pb is incorporated into rocks having U/Pb and Th/Pb ratios much larger than the mantle, and then forms a Pb mineral. This forms an anomalous lead, which requires a more complicated mathematical representation than ordinary lead.
- IV. (f). The process of mineralization from mantle fluids involves the passage of Pb through older rocks in which significant amounts of the radiogenic Pb isotopes have been produced. Mixing also yields to anomalous leads.

From just these considerations one might expect the anomalous leads to vary in isotopic composition, even within the same deposit, and be difficult to utilize for dating purposes. This is indeed the case.

A major problem in using the Pb method at all then arises. How does one recognize cases IV(b), (c) and IV(d) to use for dating the time of mineralization? R. L. STANTON (1955) and STANTON and RUSSELL (1959) have advanced a theory that lead-zinc-copper deposits of the conformable type fulfil the requirements for case IV(b). Materials of such deposits are envisaged as having formed via volcanic deposition and concentration in near-shore sediments around islands in active island areas. The volcanic source and substitution mechanism involved in Pb-emplacment by this theory imply a deep source for the Pb and little or no contact with U or Th-rich natural materials.

At any rate, assuming a homogeneous source for the lead and a single step emplacements as a Pb-ore in the crust - without contamination - we have

$$\begin{aligned}x &= a - 137.8V(e^{\lambda t} - 1) \\y &= b - V(e^{\lambda' t} - 1) \\z &= c - W(e^{\lambda'' t} - 1).\end{aligned}$$

If we can obtain values for the present day lead ratios  $a$ ,  $b$ , and  $c$  as well as for  $V$  and  $W$ , then we have only to measure  $x$ ,  $y$  and  $z$  for conformable leads and we can calculate  $t$ , the age of mineralization (knowing  $\lambda$ ,  $\lambda'$ ,  $\lambda''$ ). RUSSELL and FARQUHAR (1960) obtained the necessary parameters by making the following assumptions:

- (1) The present values of  $a$  and  $b$  in the source for conformable leads lies on the zero isochron as determined by PATTERSON (1956) in his meteorite analyses. This requires that

$$a = 1.687b - 7.97.$$

- (2) The growth curve passes through the point corresponding to analyses from Bathhurst, New Brunswick, galena in which

$$\begin{aligned}x &= 18.31 \pm .07 \\y &= 15.80 \pm .04 \\z &= 38.33 \pm .15.\end{aligned}$$

- (3) The point representing the average of the Henbury troilite and Canon Diablo troilite (9.50, 10.36) lies at one end of the growth curve.

Solving for  $a$ ,  $b$ ,  $V$  and  $t_0$ , RUSSELL and FARQUHAR (1960) obtained  $a = 18.72$ ,  $b = 15.82$ ,  $V = 0.0659$  and  $t_0 = 4.56 \times 10^9$  years.

The equations for  $x$  and  $y$  may be combined to give  $t$  as a function of  $x/y$  as follows:

$$x/y = 137.8 \frac{\frac{a}{137.8V} - e^{\lambda t} + 1}{b/V - e^{\lambda' t} + 1}.$$

This equation may be compared with the Houtermans' isochron equation in that errors in 204 measurements do not affect the age obtained. It differs in not being dependent on  $t_0$ , but  $V$  must be specified while  $a$  and  $b$  are utilized rather than  $a_0$  and  $b_0$ . To get accurate values for  $a$  and  $b$ , one may correct for errors in  $Pb^{204}$  determination. When plotted on a graph of  $x$  vs.  $y$ , samples of single stage leads with errors in the measured  $Pb^{204}$  abundances fall on a line between the origin and the point representing its true age on the growth curve. An experimentally determined pair of ratios may be extrapolated to the growth curve if the ratios are from a conformable lead (or single stage lead).

Utilizing this technique as well as some very precise lead isotope measurements on conformable leads made by KOLLAR, 1960, and OSTIC, 1962, KANASEWICH (1962) re-evaluated the constants for the Russell-Farquhar equations. He also adjusted the constants for the isochron equation to give a good check with the Russell-Farquhar equations. Fundamentally, the Houtermans isochron equation and the Russell-Farquhar equations rest on the same mathematical bases, though the models differ somewhat. Thus, they should check.

KANASEWICH (1962) obtained the following values for conformable lead from Broken Hill and Captains Flat, Australia:

	$t_0$ , b.y.	$a_0$	$b_0$	$a$	$b$	$V$	$t_1$ Broken Hill m.y.	$t_1$ Captains Flat m.y.
Isochron Eq.	4.56	9.50	10.36	-	-	-	1600	325
Conformable Eq	4.56	9.50	10.36	18.65	15.80	0.0654	1610	330

$Pb^{208}/Pb^{204}$  ratios may also be used to determine  $t_1$ , but the long half life and high primeaval abundance of  $Pb^{208}$  make the technique more difficult than for 206/204 and 207/204. With very precise  $Pb^{208}/Pb^{204}$  determination, the date may be determined, however. KANASEWICH (1962) calculated an average  $W$  from conformable lead deposits from Broken Hill, Mt. Isa, Captains Flat and Cobar, Australia using ages given by the isochron equation. Using the conformable equation, Kanasewich obtained:

$t_0$	$c_0$	$c$	$W$	$t_1$ Broken Hill m.y.	$t_1$ Captains Flat m.y.
4.56	29.49	39.25	38.21	1600 ( $z = 36.08$ KOLLAR, 1960)	360 ( $z = 38.56$ OSTIC, 1962)

### B. Anomalous Leads

KANASEWICH (1962) has considered the problem of trying to get meaningful age data from anomalous lead isotopes. Since the single stage leads (conformable) are apparently widespread, two stage leads (conformable + a single mixing or alteration procedure) would likely be common and more abundant than multi-stage leads. KANASEWICH (1962) anasewich treated the problem of two-stage leads as follows:

Consider ordinary leads differentiated from the source for conformable leads at  $t_1$  and deposited in an environment where  $U$  and  $Th$  are also incorporated. At a later time  $t_2$ , the ordinary lead is remobilized and contaminated with radiogenic lead which formed between time  $t_1$  and  $t_2$ . The lead is deposited as  $Pb$ -ore free of  $U$  and  $Th$  at time  $t_2$ . The equation for the growth curve can be written as

$$\begin{aligned}x &= x_0 + 137.8V_1(e^{\lambda t_1} - e^{\lambda t_2}) \\y &= y_0 + V_1(e^{\lambda' t_1} - e^{\lambda' t_2}) \\z &= z_0 + W_1(e^{\lambda'' t_1} - e^{\lambda'' t_2}),\end{aligned}$$

where  $V_1$  and  $W_1$  are the new values formed at time  $t_1$ , the isotope ratios of the ordinary leads in the mixture at time  $t_1$  are  $x_0$ ,  $y_0$  and  $z_0$ . Combining the ex-

pressions for  $x$  and  $y$ , we have the same form as for the growth curve of ordinary leads. That is,

$$R = \frac{y - \bar{y}_0}{x - \bar{x}_0} = \frac{(e^{\lambda t_1} - e^{\lambda t_2})}{137.8 (e^{\lambda t_1} - e^{\lambda t_2})},$$

where  $\bar{x}_0$  and  $\bar{y}_0$  are the average isotope ratios of the ordinary leads. These ordinary leads, uncontaminated, may be found, and from them  $t_1$  determined. Then  $t_2$  can be calculated using the above relationship. Furthermore, if one has no samples of ordinary lead to analyze for  $\bar{y}_0$  and  $\bar{x}_0$ , these values may be found by the intersection of the straight line with the growth curve.

One can also bring in the Th-Pb<sup>208</sup> system and utilize a plot of  $z/x$  vs.  $y/x$ . This plot eliminates Pb<sup>204</sup> (with concomitant errors) and usually gives a better straight line plot which may intersect the growth curve at  $t_2$ .

As an example, Fig. 10 shows plots of  $x$  vs.  $y$  and  $z/x$  vs.  $y/x$  for the simplest type of anomalous lead: a mixture of two ordinary leads. The samples are from the Cobalt-Larder Lake-Noranda areas of Ontario and Quebec (R. M. Farquhar-Toronto Analyses. See KANASEWICH (1962), p. 82, et seq.). Field relations show that the samples are close to the boundary between two  $P_e$  geological provinces of different age. As seen in Fig. 10, the samples fall on a chord which intersects the growth curve at  $\sim 3000$  m.y. and  $\sim 2200$  m.y. The younger lead samples fall on the chord close to 2200 m.y., while the older samples lie close to the 3000 m.y. point on the growth curve. Samples which (from field relations) are likely to be of mixed origin tend to fall nearer the middle of the chord. If the isotope ratios extended past the growth curve, a two-stage anomalous lead would be indicated, rather than mixing of two ordinary leads. The times of mineralization obtained in the plots would still be approximately valid, however.

Various types of plots may be expected for different types of anomalous leads. The time between  $t_1$  and  $t_2$  may be very small (short period - two stage) or long (long period - two stage) for two stage anomalous leads. If the second mineralization is quite young (say  $\sim 400$  m.y. ago), the date for  $t_2$  will carry a relatively large error since the plot is no more exact than for  $P_e$  leads. There is also the possibility of three-stage and higher anomalous leads. To interpret the plots of anomalous leads one must first be able to recognize them. Only insofar as a valid model for the history of the lead can be constructed is it possible to obtain meaningful dates.

### C. Criteria

With regard to the problem of recognizing various types of anomalous leads, the classification of lead isotope ratios by KANASEWICH (1962), pp. 128-131, may be quoted.

#### "Single-Stage Leads

Criteria for recognizing single-stage leads are difficult to specify and the limits given below are only tentative. The problem is being studied in detail by R. G. OSTIC (1962) and the conclusions reached here will doubtless need some

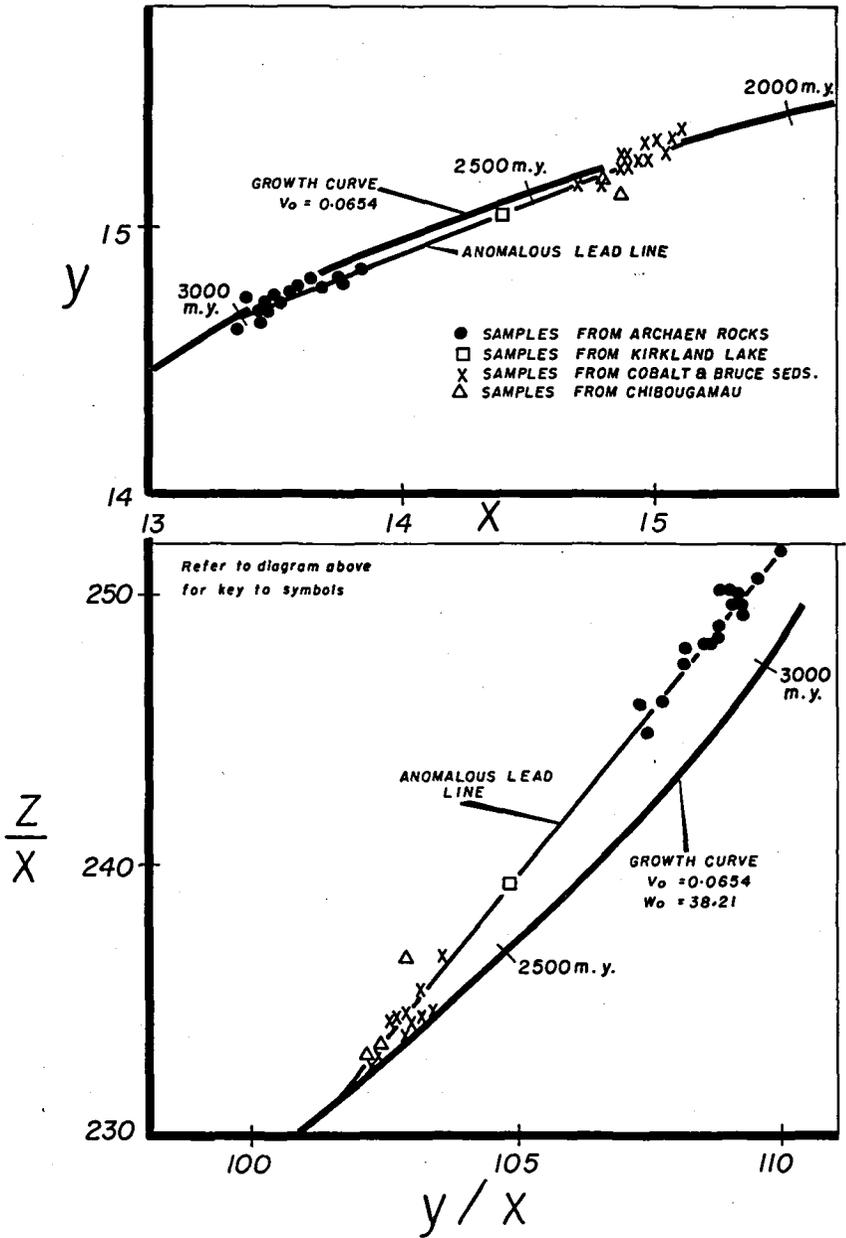


Figure 10. Lead isotope compositional diagrams for samples from the region between Cobalt, Ontario and Chibougamau, Quebec (Farquhar - Toronto Analyses) (KANASEWICH (1962) p. 83).

modification. In all cases, consideration must be given to interlaboratory differences and the amount of  $Pb^{204}$  error to be expected.

Preliminary results indicate that four factors should be considered in the specification of an ordinary lead. The limits given in brackets are for samples which have not been analyzed with intercomparison techniques.

(1) The isotopic composition of a group of ordinary leads from an area should be constant within 0.3% (1%).

(2) The  $Pb^{206}/Pb^{204}$  and  $Pb^{207}/Pb^{204}$  ratios of an ordinary lead should have a  $V_0$  between 0.0650 and 0.0658 (0.063 and 0.067).

(3) The  $Pb^{208}/Pb^{204}$  ratio of an ordinary lead should yield a  $Th^{232}/Pb^{204}$  ratio between 37.6 and 38.9 (35 and 41), calculated on the basis of a single lead-thorium-uranium system.

(4) The age of an ordinary lead should agree reasonably well with other age dating techniques. The amount of disagreement allowed will depend on the closeness of the geological setting and the method used for age determinations.

### Anomalous Leads

Leads which do not fit the criteria listed above are likely anomalous. Anomalous leads are most frequently recognized by the linear relationship of the isotope ratios on an x-y and x-z plot. The linear relationship may not be evident from samples at individual mines (Bluebell, St. Magloire), but should always be recognized when samples are considered from related areas. Anomalous leads were classified into short or long period types depending on the length of time spent in a radiogenic environment in comparison to 400 m.y. A further subdivision of distinctive types of anomalous leads and their characteristics are listed below:

#### (a) Mixture of Two Ordinary Leads

(1) A mixture of two ordinary leads will have linearly related isotope ratios. The line should intersect the "mantle" growth curve at two points and not extend beyond it.

(2) The isotope ratios of the two end points should satisfy the criteria for ordinary leads.

(3) Such mixtures will occur most frequently close to the boundary of two geological provinces.

#### (b) Two-Stage Growth Systems

(1) The isotope ratios will lie along an anomalous lead line which intersects the "mantle" growth curve at  $t_1$  and  $t_2$  with some points usually falling on the line beyond  $t_2$ .

(2) The uranium/lead and thorium/lead ratios in the second system will be highly variable but the mean values will be characteristic of a crustal system.

(3) The isotope ratios on an x-z graph may fall on several straight lines, not necessarily passing through the ordinary lead ratios. This is a result of oxidation of the uranyl ion in a crustal environment. This characteristic arrangement of

isotope ratios indicates that growth processes have predominated over mixing processes.

(4) The degree of homogeneity of the isotope ratios and the amount of complexity displayed on an  $x$ - $z$  graph is a qualitative indicator of the temperature at which two-stage leads were mineralized.

(5) Given the appropriate experimental information, it is possible to solve a two-stage growth process completely.

(c) Three-Stage System with  $V_1 = 0$

Ivigut, Greenland was postulated to be an example of this type. It is generally impossible to solve the system completely without independent information on the final period of mineralization. Useful limits may be determined for the various episodes in the development.

(d) Multi-Stage Growth System

Growth systems with three or more consecutive stages of development are probably quite rare. It was shown . . . that under appropriate circumstances they may be treated as a two-stage system to find the initial and final time of mineralization."

In order to be able to obtain reasonable plots of  $x$  vs.  $y$  and  $z/x$  vs.  $y/x$ , a large number of isotope analyses must be made. A large degree of isotope variation is desirable in order to obtain good linear plots for an anomalous lead line. After initial work, more samples must often be collected. If the spread of values is large, fewer samples may be used but often as many as ten samples are too few to give meaningful data.

In addition, one must take into account errors in lead-204 determinations. Isotopic variation on plots of  $x$  vs.  $y$  due to errors in Pb-204 determination can be detected by variation of the values along the error line (origin of  $x$  vs.  $y$  plot to the true point on the growth curve). This method of showing Pb-204 errors is only feasible, however, when the isotopic compositions of the samples are determined accurately. To be able to obtain reasonable data in applying lead isotope analyses to two-stage anomalous leads, the isotope ratios must be determined to better than a part per thousand.

## VI. Concordance, Discordance and "Updating"

### A. Violation of Basic Criteria

The major radioactive "clocks" have been discussed in terms of the fundamental criteria for use in geologic dating:

1. The rate of decay of the radioactive nuclide must be known, i.e.,  $\lambda$  must be accurately known and of favourable magnitude.
2. Sampling must be representative of a known geologic phase.
3. Analytical measurements must be able to be made accurately (essentially, parent and daughter determination).

4. Ideally, no daughter (or intermediate decay product as in the radioactive series of  $U^{238}$  to  $Pb^{206}$ ) should be incorporated or present in the phase to be dated at the time of its formation. Generally, the amount of "contaminant" daughter must be able to be determined and a correction made.
5. No gain or loss of either parent nuclide or daughter should occur after the phase (to be dated) has once formed a closed system.

If all of these criteria are satisfied, the dates given by various "clocks" for different minerals in a rock should be the same, or concordant. If the dates are not the same, or are discordant, one or more of the criteria may be violated. It is of primary importance to be able to determine which criteria are violated and to what extent. A good idea of the factors involved in producing discordant dates may be obtained by comparison of the data from different "clocks" for different minerals. In this way the general validity of each of the criteria may be assessed. A current major problem in geochronology consists in trying to definitively determine in what manner any given set of discordant dates has been produced.

The accuracy of determination of the decay constants is of fundamental significance. The decay constants for  $U^{238}$ ,  $U^{235}$  and  $Th^{232}$  are the most accurately known for the nuclear "clocks", and have been used to check and quasi "calibrate" the K-Ar and Rb-Sr clocks. In their review article, ALDRICH and WETHERILL (1958) listed rocks yielding U-minerals which gave concordant U-Pb dates. K-Ar and Rb-Sr dates of cogenetic mica were determined and compared with the U-Pb dates. In this comparison the Palaeozoic rocks gave good checks, but the K-Ar dates were 5-10 per cent low for Precambrian rocks. Rb-Sr dates tended to be higher than U-Pb for the oldest Precambrian rocks. Further detailed work by a number of laboratories has shown that the presently-accepted decay constants should give concordant dates for U-Pb, Rb-Sr and K-Ar to within a spread of about  $\pm 5$  per cent. It is very often found that K-Ar dates on micas are lower than accompanying U-Pb and Rb-Sr dates, even when no apparent disturbance to the initially-closed system is indicated. This is probably argon loss from the micas. There is at present no justification for a major revision of the decay constants, but work on refining the values continues.

Eliminating inaccurate decay constants (no. 1) as an important source of discordance, the other criteria must be examined. Concerning criterion no. 2, the geological relationships of the samples, the petrography and the paragenetic inter-relationships of the minerals must be established as a basis for interpretation. Samples should be chosen with the factors of metamorphism, weathering and suitability kept firmly in mind. Criterion no. 2 depends to an extent on criteria nos. 3, 4 and 5, and fruitful sampling is thus partly dictated by the latter criteria. Criterion no. 3 must be of general validity since only samples suitably rich in parent and daughter give sufficiently precise information. That is, meaningful data can only be obtained when criterion no. 3 is true. Similarly, if daughter contamination is serious, criterion no. 4 makes criterion no. 3 become poor or even invalid. Criterion no. 2 must be reconsidered as well, and samples chosen (if possible) in which criterion no. 4 is valid. Even if criteria nos. 1-4 are valid, criterion no. 5 may be invalid. Criterion no. 5 is the critical point in consideration of discordance. The determination

of isotopic relationships in a sample at the present time are dealt with by criteria 1-4, while criterion no. 5 raises the key problem of how outside influences may have disturbed the initially-closed system after its formation.

Thus, in the case of discordant dates, drastic violation of criteria 1-4 may often be eliminated as a major consideration. The problem of how and when the parent-daughter relations have been altered by outside agencies remains. Since cases of parent loss and daughter gain (increase in true date) have been shown to be relatively uncommon, dates are generally made lower by daughter loss. The newly-generated daughter is usually a poor geochemical "guest" in the host mineral lattice. Workers in geochronology have come to speak of "updating" (a moving upwards in the geologic column) when a system is disturbed by metamorphism or self-diffusion because the date is invariably decreased in magnitude.

### B. Differential Updating of Minerals

As might be expected, minerals suitable for dating vary in their response to forces of recrystallization or alteration. The effects of metamorphism should be observable in a "smearing-out" of a set of dates from different "clocks" on different minerals. This variation in dates must be consistent with geological and petrographical evidence. One of the first clear demonstrations of the variable effect of metamorphism in the dating of various minerals was made by TILTON, et al. (1958) on the Baltimore Gneiss. Much of the early dating in this Eastern Appalachian area consisted of K-Ar determinations on micas. These early results gave dates of 300-400 m.y. over a wide area and were thought to reflect one or both of the Taconic and Acadian orogenies. With further detailed work (TILTON, et al., (1960), HART, et al. (1962-63)) a wide difference in the response to updating of various minerals in the gneiss was found (see Table VII). The zircon in Table VII may simply be detrital and could merely indicate an old source for the initial sediments. The feldspar, however, is nonclastic and the 1100 m.y. date indicates that the gneiss probably

Table VII

Mineral ages in the Baltimore Gneiss; Baltimore, Md., and in an associated amphibolite phase of the Piedmont basement gneiss (TILTON, et al. 1958 and HART, et al., 1962-63)

Mineral	Age, millions of years					
	$\frac{\text{Pb}^{206}}{\text{U}^{238}}$	$\frac{\text{Pb}^{207}}{\text{U}^{235}}$	$\frac{\text{Pb}^{207}}{\text{Pb}^{206}}$	$\frac{\text{Pb}^{208}}{\text{Th}^{232}}$	$\frac{\text{Rb}}{\text{Sr}}$	$\frac{\text{K}}{\text{Ar}}$
Zircon	1040	1070	1120	940		
Microcline					1100	
Biotite					305	340
Hornblende						367
Diopside						328
Plagioclase						309

was formed at about that time. In the subsequent orogenic event(s), the zircon remained sensibly concordant, the microcline was not affected, but the biotite was strongly updated. The minerals in the associated amphibolite may be a product of one of the later orogenies or reflect extensive argon loss in metamorphism. There are now numerous cases in the literature showing such differential effects.

Precambrian igneous rocks are exposed in the Llano uplift in Texas, U.S.A. Since the initial dating by U-Pb (zircons), Rb-Sr and K-Ar on granite in this area showed closely concordant dates, a detailed study of possible minor variation in the dates of a single pluton was made by ZARTMAN (1962). As seen in Fig. 11, the biotite date varies while the other minerals are more closely concordant. The samples were taken from various parts of the pluton and from differing rock types.

Biotite obtained from obviously weathered granite yielded good K-Ar dates while the Rb-Sr dates were 3-10 per cent low. Biotites from pegmatites within the pluton gave low K-Ar dates on mica while the Rb-Sr dates were from 20-40 per cent lower. The relative sensitivity of biotite to updating is clearly demonstrated in this data.

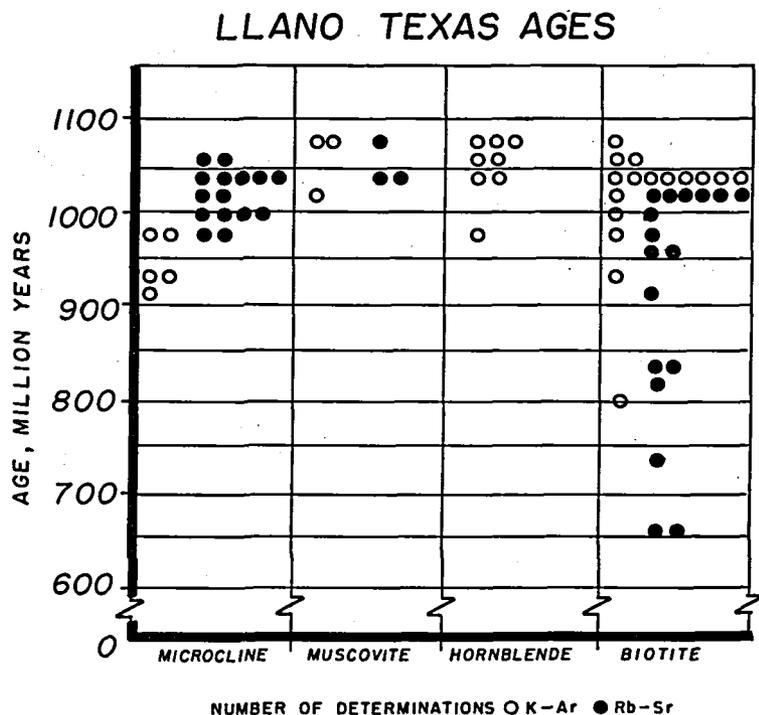


Figure 11. Diagrammatic representation of mineral ages from the Llano Uplift, Texas (ZARTMAN, 1962).

The uranium-bearing minerals also show variations in the degree to which they are updated. Pegmatitic uraninite has been shown (ALDRICH and WETHERILL, 1958) to give closely concordant dates almost all the time while more disseminated  $UO_2$ , as in Pitchblende and Thucolite deposits, tends to be discordant. Zircon shows great variability in its degree of discordance, and gives concordant results infrequently. Monazite often shows a discordance which gives ages too old to be reasonable. This pattern may be explained by postulating oxidation of  $U^{IV}$  to  $U^{VI}$  and migration of the  $U^{VI}$  out of the lattice. The Pb might be expected to remain in the phosphatic mineral, and thus an overall uranium loss occurs. This U-loss may be time-controlled if  $\alpha$ -particle bombardment progressively disrupts the lattice and aids in oxidation of the uranium. Isochron plotting ( $Pb^{206}/U^{238}$  vs.  $Pb^{207}/U^{235}$ ) helps obviate the errors in dating uranium minerals due to discordancy.

In strong metamorphism where essentially the whole mineral assemblage of a rock may be recrystallized, all the dates will change except the Rb-Sr whole rock date. When partial recrystallization or differential crystallization occurs under milder heating, the effects are less clearly evident and the problems of interpretation more difficult. The effect of mild heating on a high-grade metamorphic rock may not even be distinguishable, petrographically, but updating can occur. The variable presence of water, which enormously aids rearrangement of mineral assemblages, will have an effect similar to variation in thermal energy, with regard to updating. If controlled experiments could be performed, the parameters could perhaps be evaluated, but no laboratory experiment can take place over periods of time comparable to geologic time. The closest approximation to controlled experiments is to find a clearly defined geological setting in which nature has performed the experiment for us.

### *C. Two Examples of the Effects of Metamorphism*

#### 1. Contact Metamorphism

S. R. HART (1963) and HART, et al. (1962-63) have investigated a contact metamorphic zone in the Front Range of the Rocky Mountains in Colorado, U.S.A. where Tertiary stocks cut Precambrian metasediments yielding dates of 1200-1400 m.y. The following descriptive data is that of HART (1963). The criteria considered in choosing the location were: (1) well-exposed contact, (2) fresh unaltered rock, (3) country rock with a wide compositional variation so that many different minerals could be tested, (4) accessibility to a traverse of suitable length, and (5) an intrusive of simple geometric shape. Hart selected a granitic stock about two miles wide near Eldora, Colorado. This stock has steeply dipping sides and intrudes country rocks consisting of gneisses, schists and amphibolites. The dominant rock type is quartz-feldspar-biotite gneiss, and the rather uniform grade of metamorphism is characterized by rocks of the sillimanite-almandine subfacies of the almandine-amphibolite facies. Orogenic activity during Laramide time apparently consisted mainly of broad arching, faulting and intrusion of stocks in the old country rocks. There is no evidence for any regional thermal metamorphism since Precambrian time.

Samples were collected at intervals along an E-W line from the intrusive

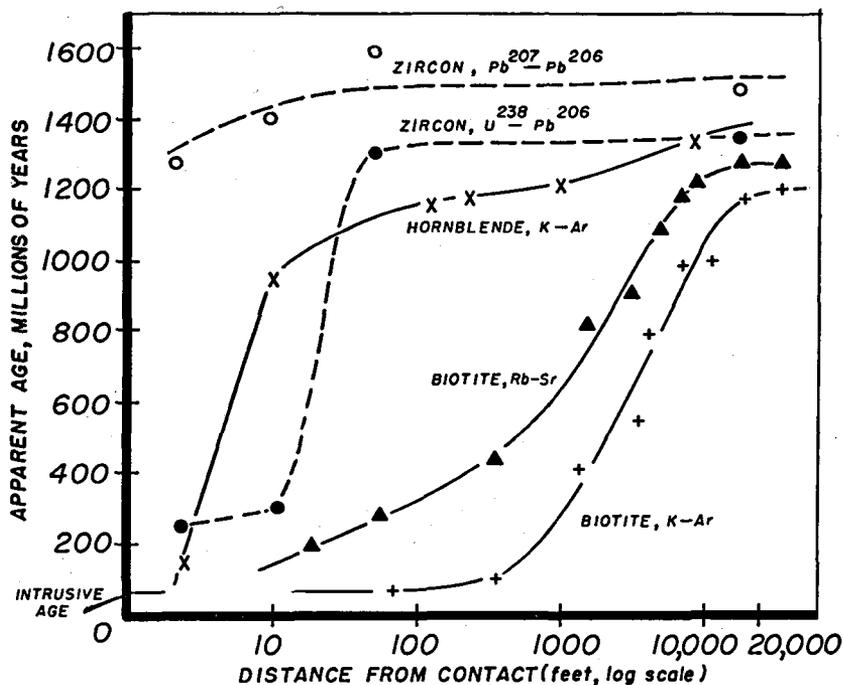


Figure 12. Variation in measured age with distance from an intrusive contact at Eldora, Colorado for zircon, biotite and hornblende (HART, et al. 1962-63).

contact out to approximately 22,000 feet (two intrusive widths). Little mineralogical alteration or variation in the country rock was observed since the country rock was already high-grade and the heterogeneity of the rocks makes effects less noticeable. Only a single sample near the contact showed hornblende altering to biotite and twinned oligoclase with untwinned sodic overgrowths. Biotite showed a faint colour change (no correlation with  $\gamma$ -index) which varied with the abundance of rutile inclusions. Biotites beyond 3000 feet from the contact were clear and free of rutile, those at 1000-2000 feet contained the most rutile and those nearer the intrusive rather less rutile. Hart postulates a possible titanium exsolution from biotite under mild contact metamorphism.

There is a very sharp transition from monoclinic feldspars at about 100 feet from the contact to triclinic feldspars outside of this zone. This is apparently a direct transition and shows little gradational change. The transition is complete within a 60-foot zone. Up to 1500 feet from the contact the homogenized bulk composition of the feldspars (Or-Ab) gave only a  $\pm 5$  per cent variation. The feldspar composition (Or-Ab) bears no relation to structural state or distance to the intrusive contact. The microcline shows uniformly well developed perthitic structure, while orthoclase shows progressive homogenization of inherited perthite as the contact is approached. At 20 feet from the contact orthoclase is faintly perthitic, and at two feet the orthoclase appears optically homogeneous but has some submicroscopic perthite (shown by X-ray data).

Hart determined the age of the intrusive as 55 m.y. on coarse biotite and 54 m.y. on fine biotite (hornblende present). The coarse biotite yielded a Rb-Sr date of  $60 \pm 9$  m.y. The results from dating a wide variety of samples from the traverse in the country rock are shown in Fig. 12. The differential response of the various "clocks" in the different minerals is clearly seen. Since argon is lost from K-feldspar even without apparent thermal effects, K-Ar for K-feldspar has been omitted. The common Sr contamination is very high, but approximate Rb-Sr ages for the K-feldspars indicate a date of 1400 m.y. or more for all samples 10 feet or more from the contact. Thus, the Rb-Sr "clock" in the K-feldspars is about as difficult to reset as the K-Ar "clock" in hornblende. In addition an isochron plot for Rb-Sr in the K-feldspars shows marked deviations from a straight line, indicating possible gain of  $\text{Sr}^{87}$  (ratios apparently too high). A concordia plot of the zircons gives an episodic loss pattern with  $t_1 = \sim 1600$  m.y. and  $t_2 = \sim 75$  m.y., in accordance with the other age data. Another factor not indicated in Fig. 12 is that of grain size. If diffusion of the daughter element under thermal heating is important, then grain size should be a factor in determining the degree to which a mineral may be updated. Hart found that finer-grained biotite than that used for the biotite K-Ar plot in Fig. 12 plotted further to the right. This indicates simply that the finer-grained the mineral, the more rapid or complete will be its response to alteration or updating. This factor may be a partial explanation for cases reported in the literature where a pegmatite (cutting a fine-grained country rock) gives older dates than the country rock for the same minerals.

## 2. Regional Metamorphism

The detailed surface mapping and study of the Precambrian Shield in north-east Alberta by the Research Council of Alberta offers an excellent test of usefulness of radioactive dating in an area of extensive metamorphism. In the area under consideration, about 350 square miles around Andrew Lake, are four groups of rock types: an old basement complex; relatively unmetamorphosed sediments; massive-leucocratic and -biotite granites; and foliated porphyroblastic granites. The old basement complex comprises biotite and hornblende granite gneisses, high-grade metasedimentary rocks, foliated granites, and mylonitic zones. The relatively unmetamorphosed sedimentary rocks (mainly greenschist facies) are composed of silty graywackes, which show clastic textures and graded bedding where well preserved, as well as a lesser amount of "intermediate" extrusive rocks showing ophitic and trachytic textures. Very likely these low-grade metasedimentary rocks represent a period of deposition later than that of the high-grade metasediments of the basement complex. The massive-leucocratic and -biotite granites intrude most other rocks, whereas the foliated porphyroblastic granites seem to be metamorphic equivalents of the low-grade metasediments. The field relations suggest two, and possibly three, orogenic events in this region.

Reconnaissance K-Ar dating of the principal rock types gave a range of mica dates from 1740 to 1830 m.y. (GODFREY and BAADSGAARD, 1962). With further work, 28 mica K-Ar dates yielded a mean value of  $1810 \pm 20$  m.y., though the geology of the area indicates a much larger possible spread in the

Table VIII

U-Pb, Th-Pb Ages, Andrew Lake Area, Northeast Alberta Precambrian Shield

Sample No.	Rock and Mineral Used (Petrographic term)		Ages, millions of years			
			Pb <sup>206</sup>	Pb <sup>207</sup>	Pb <sup>207</sup>	Pb <sup>208</sup>
			U <sup>238</sup>	U <sup>235</sup>	Pb <sup>206</sup>	Th <sup>232</sup>
151-11	Granite boss (quartz monzonite)	Zircon	1320	1600	2000	1330
128-5	Basic plug (hybrid granite)	Zircon	1540	1680	1860	1530
729-3	Massive granite intrusive (granodiorite)	Zircon	1390	1580	1850	1530
729-4	Older granite (quartz monzonite)	Zircon	1230	1430	1750	....
90-2	Porphyroblastic granite gneiss (composite) (quartz monzonite gneiss)	Allanite	1850	1840	1820	1880
		Allanite	1990	2000	1960	1930
		Zircon	1870	2020	2190	1950
44-1	Mineralized biotite schist (granodioritic pegmatite)	Uraninite	1410	1570	1800	1090
		Monazite	2290	2120	1950	1880
149-1	Granite gneiss-basement complex (quartz monzonite gneiss)	Zircon	1540	1840	2200	1500

true age of the various rock units. The value of 1810 m.y. may be regarded as the time of the latest metamorphic event in the area.

The minerals listed in the Table VIII were separated and the U-Pb ages determined. Very little zircon was recovered from samples of the low-grade metasediments. Despite discordance, the Pb<sup>207</sup>-Pb<sup>206</sup> ages definitely indicate primary crystalline material older than 1800 m.y. in the area. The U-Pb data are plotted on a concordia diagram in Fig. 13, although the minerals are from a variety of stratigraphic positions and rock types. Since the 1810 m.y. mica dates apparently rule out an episodic lead-loss discordance, curves are calculated and plotted for loss of lead by continuous diffusion (TILTON, 1960) for 2270 and 1920 m.y. The uraninite and monazite are apparently cogenetic. The 1920- and 2270 m.y. diffusion ages probably delineate two events involving magmatic crystallization, provide clues to the source of the metasediments, but do not aid in specifying the time of sedimentation.

Table IX gives Rb-Sr ages for four feldspars and model lead ages for two of the four feldspars plus a galena. These data also indicate that the geologically older rocks are more than 1800 m.y. old. In addition, four K-Ar hornblende ages for these rocks were from 1850 to 1930 m.y. The hornblendes appear to have been affected to a lesser degree than the biotites by the last metamorphic event (HART, 1961). If an older Rb-Sr age for the feldspars has not been affected by later metamorphism, the model lead ages should be comparable. The data for 149-1 and 90-2 feldspar seem to indicate partial alteration, to judge from the 2270-m.y. zircon diffusion age. The galena is evidently a product of the later 1920-m.y. event.

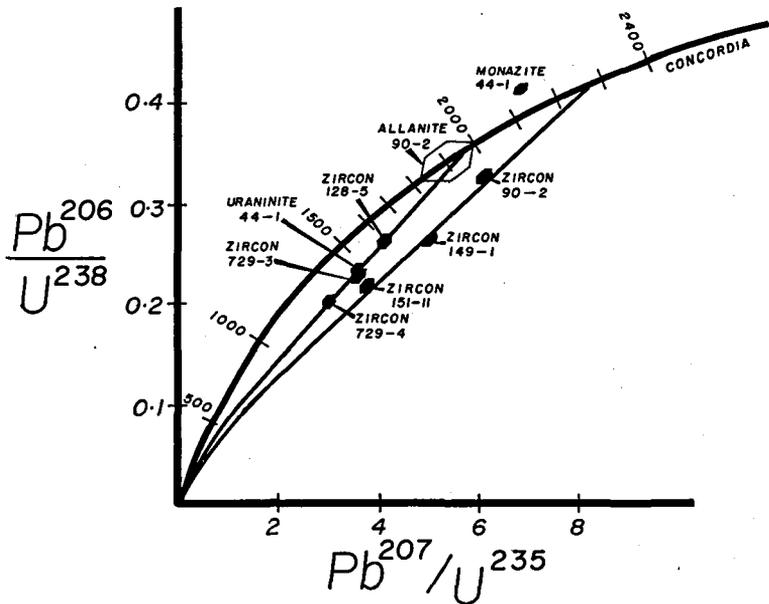


Figure 13. Parent-daughter ratios for uranium-bearing minerals from the Andrew Lake area, northeastern Alberta, compared with two curves calculated for loss of lead by continuous diffusion for 1920 and 2270 m.y.

Table IX

Mineral Ages from the Andrew Lake Area, Northeast Alberta Precambrian Shield

Sample No.	Rock and Mineral (Petrographic term)	Ages, millions of years			
		Rb-Sr	Pb Model Ages (Russell-Stanton-Farquhar)		
			208/204	207/206	
151-11	Granite boss (quartz monzonite)	K feldspar	1800 ± 300		
729-4	Older granite (quartz monzonite)	K feldspar	1850 ± 150		
90-2	Porphyroblastic granite gneiss (composite)	K feldspar	2220 ± 100	1570	2160
149-1	Granite-gneiss, basement complex (quartz monzonite gneiss)	K feldspar	2060 ± 150	-120	2020
1-3	"Younger" metasediments, mineralized (orthoquartzite)	Galena		3600	1890

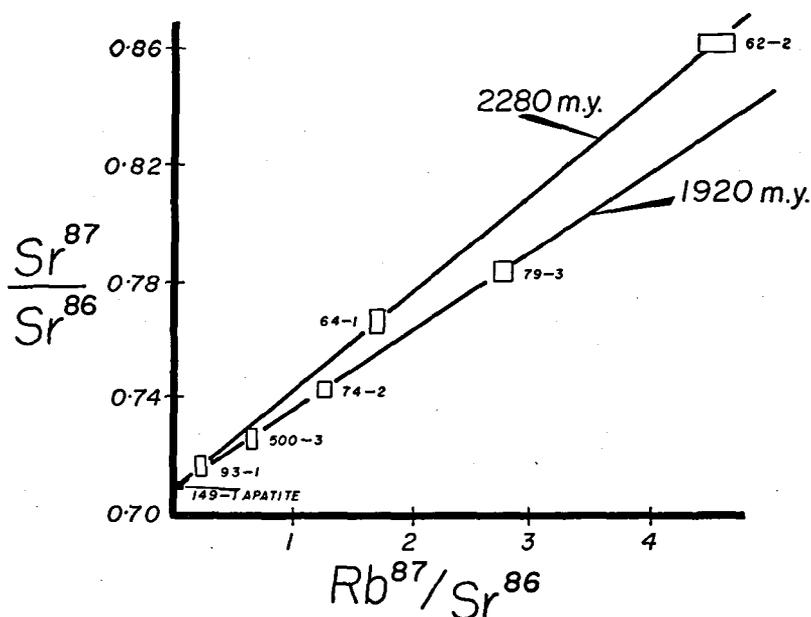


Figure 14. Plot of  $Sr^{87}/Sr^{86}$  ratios versus  $Rb^{87}/Sr^{86}$  ratios for six whole-rock samples and one apatite from the basement gneiss complex of the Andrew Lake area in northeastern Alberta.

Whole-rock rubidium-strontium ages for six samples of granite gneiss from the basement complex have recently been determined at the University of Alberta; Fig. 14 presents the data in an isochron plot. The somewhat surprising division of the samples between two isochrons indicates that the basement complex is directly or indirectly involved in both the events given by the U-Pb data. The dual division is not easily explained, despite abundant field evidence of gneissic xenoliths in a gneissic matrix. For example, in sample 149-1, apatite has  $Sr^{87}/Sr^{86} = 0.711$ ; feldspar gives 1850 m.y., zircon, 2270 m.y.; biotite, 1790 m.y. The apatite should have picked up some extra radiogenic  $Sr^{87}$  in the later metamorphic events, but it is possible that the apatite used (200 mesh) represents unaltered detrital apatite rather than mixed apatite (apatite not affected?).

Some preliminary conclusions are:

1. Two primary magmatic events occurred about 1900 and 2300 m.y. ago in the Andrew Lake area.
2. Both these source materials appear in the gneissic or metasedimentary phases of the basement complex and are thus older than the massive-leucocratic granites.
3. The massive-leucocratic and biotite granites, young according to field relations, are very close in age to the "younger" portions of the gneissic basement complex.

4. The latest metamorphic event (1810 m.y.), as given by the K-Ar mica dates, likely accounts for much of the obscuring of the field relations between the two earlier events.

#### D. General Comments

Utilizing data such as that of HART, et al. (1962-63) and many other published observations of updating and discordance, a crude relative scale of response to forces of updating may be outlined. Table X is merely a general guide, and the relations vary somewhat in different geologic situations.

Research workers in geochronology are still in the midst of trying to unravel the complexities of updating. To say that thermal updating is the only important factor is certainly incorrect. The relative role of dynamic metamorphism is as yet speculative. Furthermore, the wide variations in the intensity and nature of metamorphic events indicates there are multiple possibilities for patterns of discordance. The rate and degree of chemical alteration or recrystallization will vary with differences in factors such as temperature, pressure, composition and presence or absence of fluids (water). Extremely slow rearrangements of composition involving diffusion of elements are effective in updating minerals even when they proceed to a degree of completion that may not be distinguishable by petrographic or X-ray methods of observation. On the other hand, the possibility of using isotopic variation to study these ultra-slow processes arises. It should be possible to work out tests for chemical equilibrium in rocks, utilizing the isotopic balance of radiogenic daughters. In dating any group of rocks, however, each case must be considered on its own merits and drawbacks as well as in the light of the current "state of the art" of geochronology.

Table X

Approximate relative order of the ease of producing discordance in various nuclear clocks in different minerals

	K-Ar	Rb-Sr	U-Pb	Pb <sup>207</sup> -Pb <sup>206</sup>
↓ decreasing ease of updating ↓	K-feldspar Glauconite Sylvite		Allanite Uraninite	
	Lepidolite Biotite Sanidine	Lepidolite Biotite	Monazite Zircon	
	Muscovite	Muscovite		Allanite Uraninite Monazite Zircon
	Hornblende Pyroxene	K-feldspar		
		Whole Rock		

## VII. The Dating of Sedimentary Rocks

The interpretation of radiometric dates may be more complex for sedimentary materials than for igneous and metamorphic rocks. Does the date indicate time of sedimentation, time or period of diagenesis or alteration, time of original formation of the minerals in the sediment (source rocks), subsequent metamorphic effects or a combination of one or more of the preceding possibilities? The key factor is the time of formation of minerals amenable to dating. If the minerals are detrital, the date indicates an approximate time of formation of the source rocks. If chemical processes accompanying the deposition of the sediments form new minerals, the time of deposition may be dated using these minerals. If extensive and prolonged diagenesis forms new minerals, an estimate of the time of main diagenetic action may be obtained. Subsequent metamorphism may reset or obliterate the above possible dates.

The time of deposition is the most often desired date, especially for purposes of stratigraphic correlation or time scale work. The application of dating methods towards this end is limited mainly by the occurrence of suitable minerals. Accordingly, the dating of sedimentary rocks will be discussed in terms of the materials that have been used to estimate the time of deposition of the sediments.

### A. Evaluation of Materials

#### 1. Glauconite

Because of its authigenic origin and wide distribution glauconite has been extensively studied, mainly by the potassium-argon method. It was initially thought that glauconite might give high K-Ar dates because of detrital mica nuclei within the pellets. However, very few obviously high glauconite dates have been obtained. Instead, glauconite appears to either lose argon or gain potassium to give the large proportion of apparently low dates reported in the literature. EVERDEN et al. (1960) sampled a well-defined Eocene horizon at the surface and at depths down to 12,000 feet in boreholes. The deepest sample lost about 60 per cent of its radiogenic argon relative to the surface samples, with intermediate losses at intermediate depths. The high sensitivity of glauconite to argon loss has also been demonstrated in the laboratory by AMIRKhanov, et al. (1958) and POLEVAYA et al. (1960). Evolution of radiogenic argon begins at 200–300°C and is complete at 500–600°C. Though it appears that small temperature increases and/or pressure changes can affect the argon content of glauconite, some authors believe that glauconite with a satisfactory burial history can give reliable dates. This is substantiated by the time scale and Precambrian glauconite dates reported by POLEVAYA (1960). In a large number of other areas, however, glauconites give discrepant data with the K-Ar dates invariably being low. Glauconite taken from the same mid-Cretaceous stratigraphic marker horizon in five separate Alberta, Canada, oil wells at essentially the same depths gave dates varying by 35 per cent although the sample preparation was identical. In an extensive study, HURLEY, et al. (1959) found that in general glauconite yields K-Ar and Rb-Sr dates that are often very close to estimated true ages but are usually slightly low or badly off the mark. The

relatively high proportion of contaminant Sr in most glauconites limits the application of Rb-Sr dating to Paleozoic and older samples. Rb-Sr dates tend to follow the K-Ar dates rather well, and the factors which cause discrepant dates seem to affect both nuclear clocks in a similar manner for the most part. There are at present no certain criteria for predicting the reliability of any given glauconite sample.

In general younger glauconites have a higher proportion of expandable layers than older glauconites, which tend to have higher potassium content and possess "well-ordered" lattices (BURST, 1958). HURLEY, et al. (1959) suggest that glauconite pellets may continue to develop into purer mineral grains over long periods of time with the roughly 30 per cent expandable layers in young glauconite decreasing to about 10 per cent in samples of early Paleozoic age. Argon or Sr<sup>87</sup>\* generated in the expandable layers might be expected to be partially or wholly lost in the rearrangement of the lattice.

## 2. Bentonites

Since bentonite horizons are often of great lateral extent and stratigraphically well-correlated, they offer an excellent opportunity for the radiometric dating of the time of sedimentation. Derived from explosive vulcanism, single bentonite bands represents an exceedingly short period of geologic time, and are usually negligibly contaminated with normal detrital sedimentary materials. The radiometrically-useful minerals biotite and sanidine are commonly found in bentonitic clays, and are unlikely detrital contaminants. If an unfolded bentonite-ash horizon is in the form of easily disaggregated clay, metamorphism can have played little or no part in rearranging parent-daughter relationships in the datable minerals, while leaching and weathering seem to change the parent-daughter ratios only in the most extreme cases.

The potassium-bearing volcanic materials such as sanidine, biotite, low-K feldspar, illitic clay, and volcanic glass are affected to a different extent in weathering and diagenesis. Their abundance and usefulness depends upon their resistance to chemical changes and the nature of the volcanic source material. These five materials will be briefly considered below.

### a. Sanidine

The presence of sanidine in a bentonite is indicative of the high temperature origin of the bentonitic materials. The sanidine is usually in the form of clear, anhedral fragments of low 2V and contains relatively few inclusions. Detrital microcline and orthoclase contamination is easily identified in the separated material, but is only very rarely found. Sanidine loses little or no argon compared to microcline, has a very low level of contaminant air argon, and is eminently suitable for K-Ar dating. There is some evidence (BAADSGAARD et al., 1961) that sanidine in volcanic flows may be affected by retrograde metamorphism in the cooling of the flow. Sanidine from flat-lying, plastic bentonite beds is rarely twinned, and gives dates which almost always check with those from fresh cogenetic biotite. With very few exceptions, dates from bentonite sanidine have checked with available geologic and radiometric evidence for the relative age of the strata.

#### b. Biotite

Biotite commonly occurs in bentonite beds, often together with sanidine, in the form of fragments, hexagonal plates and thin books.

The problem of leaching and alteration of initially-deposited biotite may be evaluated by comparing data obtained for cogenetic, fresh sanidine with data from various fractions of biotite. It is generally found that regardless of the degree of leaching of potassium (and Fe) from the biotite, the Ar/K ratio stays essentially unchanged. In rare cases a very highly altered biotite may give a slightly lower Ar/K ratio than for accompanying sanidine (the order of five per cent), but the variations noted are generally within analytical error. Utilizing magnetic separation, biotite in quantities as low as a few parts per million in bentonite may be separated for dating.

#### c. Low-K Feldspars

The plagioclase present in large quantities in many bentonites may also be utilized for K-Ar dating. The use of high temperature low-potassium feldspars has yet to be checked for bentonitic materials, but would offer a third phase for dating. In some bentonites, it would form the only datable phase. Difficulties in utilizing low-K material would center about the small amount of argon present in the younger material. The potassium could be determined accurately by isotope dilution, but a highly sensitive mass spectrometer and a very clean argon extraction procedure are necessary.

#### d. Potassium-bearing Clay Minerals

The bentonitic clay matrix may contain from 2 to 4 per cent  $K_2O$ . The clay minerals may be montmorillonitic, illitic and occasionally kaolinitic, but very frequently one gets mixed layer clay minerals. From the few data on sanidine, biotite and clay matrix from single bentonites, it appears the clay yields dates which are from 15 to 20 per cent low. This is perhaps a surprising retentivity, but makes the effect of clay contamination in the biotite and sanidine less severe than might be expected.

#### e. Volcanic Glass

The occurrence of volcanic glass in plastic bentonites is actually quite rare, since the glass and fine ash break down to yield clay minerals. When present, the glass is difficult to separate cleanly, since it usually contains numerous inclusions of the various accompanying minerals. Even when relatively pure shards may be obtained, the argon leakage is apparently very severe: the few bentonitic glasses run at the University of Alberta (unpublished) have given dates one-half or less of the Holmes time-scale equivalent of their assigned stratigraphic age.

There are a number of general drawbacks in utilizing bentonites for dating sedimentary time horizons. The vertical distribution of bentonites is erratic in that a part of the geologic column in a given area may contain abundant beds while the major portion of the column is barren of usable bentonitic material. Even if bentonites are present, the datable minerals may be too sparse, too

badly altered, or missing entirely. The internal criteria for testing contamination of a bentonite bed are not clearly defined, and detrital K-feldspar is almost impossible to separate from sanidine. A few grains of a Precambrian feldspar can significantly affect the date given by a Tertiary sanidine. In areas where extensive faulting, folding and thrusting have occurred it is no longer safe to assume the bentonitic minerals have not been significantly affected for the purposes of dating.

### 3. Shales

EVERNDEN et al. (1961) reported K-Ar dates on ten shales of known stratigraphic age. Three of the results were within 5 per cent of a control time-scale based on igneous material while five were within 10 per cent. These authors suggested that the potassium-bearing mineral(s) in the shale were largely authigenic and retained argon adequately. The problem of defining the K-bearing material in shale was further pursued by HOWER, et al. (1963), who showed that coarser Paleozoic shale particles gave K-Ar ages much greater than the time of deposition while the finest particle sizes yielded ages that were too low. The coarser particles giving too old ages were found to be rich in well ordered 2M illite or muscovite while the low ages were from materials containing a higher proportion of 1 M<sub>4</sub> illite. The 1 M<sub>4</sub> illite is likely authigenic, but retains argon poorly. The K-Ar data of EVERNDEN et al. (1961) may be explained as an approximate cancelling out of opposing systematic errors.

COMPSTON and PIDGEON (1962) made Rb-Sr measurements on three Australian shale formations and found that the data suggested that whole rock Rb-Sr dating of shales can be a useful and accurate method of dating sediments. Work by WHITNEY and HURLEY (1963) indicates that the presence of inherited radiogenic strontium in detrital minerals forms the major source of error in Rb-Sr dating of whole-rock shale samples. Their study showed that where the provenance of the detrital material is from rocks relatively close in age to the time of sedimentation or where unweathered detritus is small in amount, the maximum Rb-Sr whole rock date of the shale may be close to the true age. The applicability of Rb-Sr whole rock dating is likely to be most fruitful only in old unfossiliferous sediments. In these older sediments the problem of much older detritus is greatly lessened and the relative proportion of radiogenic strontia in the samples is generally enhanced.

COBB (1961) has made a study of the U-Pb dating of bituminous marine shale. In detailed work on the Swedish Kolm, it was found that loss of an intermediate in the U<sup>238</sup> series best explains the strongly discordant dates. Cobb concluded that the major cause of discordant U-Pb dates on black shales is ground-water leaching. If only U<sup>238</sup>/Pb<sup>206</sup> dates are obtainable, they are likely minimum values, and the common lead correction is usually so large that post Paleozoic samples are difficult to utilize.

### 4. Sylvite

The very high potassium content of pure sylvite makes both the K-Ar and K-Ca "clocks" applicable, since relatively little contaminant calcium is present in good samples. Unfortunately, the Rb-content of sylvite is too low to give

good Rb-Sr data. INGRAM et al. (1950) used pure Stassfurt sylvite to determine the radiogenic argon/radiogenic calcium ratio. Their value, 0.126, agrees well with the presently accepted value found by counting methods. The relative ease with which sylvite is recrystallized and the scarcity of samples makes this material only occasionally useful. POLEVAYA, et al. (1958) determined both K-Ar and K-Ca dates for three sylvites and found that recrystallization caused strong argon loss while the K-Ca dates were apparently unaffected. Unpublished University of Alberta data on a Devonian sylvite from the Elk Point formation, Saskatchewan, indicates an argon loss of at least 50 per cent. In general sylvite is poor material for K-Ar dating unless recrystallization effects can be shown to be absent.

## 5. Fossils

If fossils could themselves be dated, it would be a large step forward in establishing time scale correlations. LIPPOLT and GENTNER (1962) have attempted to date fossil materials by the K-Ar method, using fossil bone, limestone and fluorite. Their results were all much lower than accepted time-scale dates except for a specimen of Triassic bone ( $188 \pm 10$  m.y.).

Ar-diffusion experiments suggested poor argon retentivity for the fossil samples and it was concluded that the fossilization process is decisive in the K-Ar dating of these materials.

## B. Applications

There are numerous applications possible if a stratigraphic horizon can be dated reasonably accurately, and a few that have been and are being studied will be mentioned.

The establishment of a Post Cambrian geological time scale is continuing, and its value needs little elaboration. More refined work needs to be done in establishing critical boundaries between periods and in the delineating of epochs. The formulation of a time-stratigraphic division of the Precambrian will be difficult, and metamorphic events are already being used to divide up the Precambrian into "time-event" units, but these events may eventually prove to be too diffuse or drawn out to provide suitable time demarcations.

If a series of conformable sediments contains horizons that are datable, the rate of sedimentation (in terms of compacted and indurated sediments) may be estimated. This is best done in the Mesozoic and Cenozoic where the error in the date on a horizon will be a smaller absolute number than for older horizons. Rates of  $\sim 150$  feet/m.y. have been found in the Cretaceous of the Western Canadian sedimentary basin (FOLINSBEE, et al. 1961).

Provenance studies are possible utilizing detrital minerals in sediments. Detrital feldspar in sandstones may be used to distinguish between two sources of widely differing age despite the argon leakage from feldspar (WILLIAMS, et al., 1962). Detrital muscovite also may be utilized despite the variable effects of weathering provided there is little multisource mixing and the sources differ in age sufficiently.

LEAKEY, CURTIS and EVERNDEN (1962) have utilized K-Ar dating of volcanic

ash horizons to date horizons of anthropological significance in the Olduvai Gorge in Africa. In this case dating established that fossil man dates back at least two million years – much older than had been thought.

The dating of volcanic sills and flows encountered in oil well drilling can help evaluate further oil possibilities for a particular hole or in a certain region.

When more is known about the detailed behaviour of radiogenic daughter elements in various minerals, it should be feasible to attack some problems of diagenesis by studying the distribution relationships of radiogenic elements in diagenetic minerals. The length of many diagenetic processes may be assessed and possible details of the chemistry elucidated.

With increasing accuracy of dating, it is possible that the rate of evolution of many fossil species may be estimated. Rates of migration for free moving marine forms would be interesting data as well.

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