Rb-Sr ISOTOPIC STUDIES RELATING TO PROBLEMS OF GEOCHRONOLOGY ON THE NELSPRUIT AND MPAGENI GRANITES.

Thesis submitted for
the degree of
MASTER OF SCIENCE
at the
University of the Witwatersrand

by
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July, 1967

STATEMENT

The work contained in this thesis was performed by the author during the period January 1966 to May 1967.

The samples marked OG were previously investigated by Dr. H.L. Allsopp (the author carried out some of the duplicate measurements).

The samples marked AA were collected by the author and Dr. Allsopp under the guidance of Professor L.O. Nicolaysen. The other samples were collected by Professor Nicolaysen and Dr. Allsopp.

All other work, except where acknowledged, was performed by the author.

(signed) A.A.A. de Gasparis

Acknowledgements

I am grateful to Professor L.O. Nicolaysen and Dr. H.L. Allsopp for their invaluable guidance, and especially to the latter for his advice on, and supervision of, the experimental work. I had many helpful discussions with Mr. M.J. Viljoen and Mr. R.P. Viljoen, Mr. C. Anhaeusser and Dr. C. Roering on the geology of the Barberton Mountain Land. Mr. R. Davies helped me with the mineralogy and gave me advice on the description of thin sections and the recognition of minerals. Mr. M. Albertyn collected a number of hand specimens from which it was possible to gain an approximate idea of the Rb-Sr distribution in the migmatite; this aided planning of the field trip to collect samples. Mr. J. Swinley assisted in operating the equipment and in the crushing of samples.

I am indebted to the Economic Geology Research Unit for allowing the use of maps 1 and 2 which were compiled for the paper of Anhaeusser et al. (1967).

I am grateful to the South African National Committee for the Upper Mantle Project which sponsored this investigation.

I would like to thank my wife Priscilla for the typing of this thesis and the assistance she gave me.

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CHAPTER I - THEORY AND METHODS OF GEOCHRONOLOGY

1. RADIOACTIVE DECAY

The mode of radioactive decay is expressed quantitatively as follows:

if N is the number of atoms of a given radioactive element, the decay rate will be:

$$-\frac{dN}{dt} = N\lambda$$

where λ is the decay constant and indicates the fraction of atoms that are transformed in unit time.

Integrating:

$$\log \frac{N_t}{N_o} = -\lambda t$$

or:

$$N_t = N_o e^{-\lambda t}$$

which is the law of transformation.

The time in which a certain number of radioactive nuclides of a given element are halved by nuclear transformation is called the half-life of the element.

2. GEOCHRONOLOGY

It has been proved that the decay rate of radioactive nuclides with short half lives is not influenced by any physical condition like pressure, temperature, magnetic field etc. It has been postulated that this can be applied to the decay of radioactive nuclides with long half lives and that therefore the decay rate of these nuclides has not changed in spite of varied physical conditions during geological time.

The time since a rock or a mineral phase has remained a closed chemical system can be estimated by using the rate of decay of a long lived radioactive nuclide from the present-day measurement of the abundances of the parent and daughter

nuclides.

This technique has been called geochronology (from the Greek words: γῆ - the earth, χρόνος- time, λόγομαι - to know), a term first used by Williams (1893) for his calculations of geological ages from thicknesses of sediments.

A few years before the second world war the introduction of mass spectrometry and the work of Nier and his associates gave tremendous impetus to geochronology and isotope geology. Since then many methods of absolute dating have been devised and ages have been calculated using decay schemes of a number of radioactive nuclides. The most commonly used decay schemes are: U^{238} - Pb^{206}, U^{235} - Pb^{207}, Th^{232} - Pb^{208}, Rb^{87} - Sr^{87} and K^{40} - Ar^{40}. These elements are present in most of the crystalline rocks of the earth's crust and their long half lives are known with sufficient accuracy.

A brief description of the U, -Th, - Pb method

The nuclides U^{235}, U^{238} and Th^{232} decay respectively to Pb^{206}, Pb^{207} and Pb^{208} by a complex series of nuclear transformations but, because the half lives of the parent isotopes are so long compared with those of the other members, the transformations U - Pb and Th - Pb can be considered as simple ones and the time calculated using only one value of the half life.

Disregarding the various intermediate stages, the transformations of U and Th to Pb can be represented as follows:

$$U^{238} \text{ --------- } Pb^{206} + 8He^{4} + \sigma \qquad (1)$$
$$U^{235} \text{ --------- } Pb^{207} + 7He^{4} + 4 \qquad (2)$$
$$Th^{232} \text{ --------- } Pb^{208} + 6He^{4} + 4 \qquad (3)$$

if λ', λ'', & λ''' are the decay constants of the transformations (1), (2) and (3) respectively, from the law of transformation we have:

$$N(Pb^{206}) = N(U^{238}) \quad (e^{\lambda' t} - 1) \qquad (i)$$
$$N(Pb^{207}) = N(U^{235}) \quad (e^{\lambda'' t} - 1) \qquad (ii)$$
$$N(Pb^{208}) = N(Th^{232}) \quad (e^{\lambda''' t} - 1) \qquad (iii)$$

where $N(Pb^{206}, Pb^{207}, Pb^{208})$ represent the number of atoms of radiogenic lead, and $N(U^{238}, U^{235}$ and $Th^{232})$ represent the present day number of atoms of parent element. Th and U minerals generally contain original lead that is not radiogenic. The presence of this original lead is indicated by the non-radiogenic isotope Pb^{204} and thus corrections for original lead must be applied to the equations (i), (ii) and (iii).

From the combination of (i) and (ii):

$$\frac{N(Pb^{207})}{N(Pb^{206})} = \frac{e^{\lambda''t} - 1}{e^{\lambda't} - 1} \cdot \frac{N(U^{235})}{N(U^{238})} \qquad \text{(iv)}$$

the values of t obtained from (iv) are called lead-lead, lead ratio, or Pb^{207}/Pb^{206} ages.

Equations (i), (ii), (iii) and (iv) yield three independent values of t; the values so obtained should all be equal under ideal conditions, that is if the mineral examined has remained a chemically closed system in respect to U, Th and Pb, if the radioactive equilibrium has been maintained throughout the life of the mineral, and if the constants λ', λ'', & λ^* are correct. In most cases identical ages are not obtained - the ages are then said to be discordant. The simplest reason for discordant ages is the loss of radiogenic lead or radioactive parent by leaching or slow diffusion.

Leaching effects are shown in figs. 1 and 2. From the figures it is evident that the Pb^{207}/Pb^{206} age is in all cases the closest to the true age. The only reason to suspect lead ratio ages would be selective leaching of one of the two isotopes 207 or 206 (fractionation), but because of their very close mass value and identical chemical properties natural fractionation seems unlikely.

The usefulness of lead ratio ages is limited to precambrian rocks, because (as can be seen from fig. 3) the ratio Pb^{207}/Pb^{206} varies very little for young minerals.

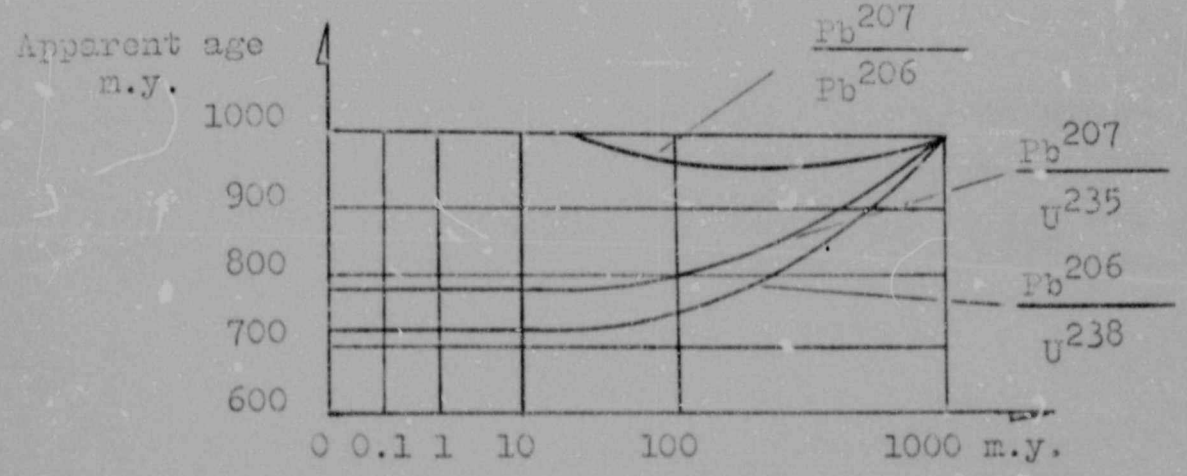


Figure 1: Effect on apparent ages for leaching of 30% of lead at various times from a 1000 m.y. old mineral

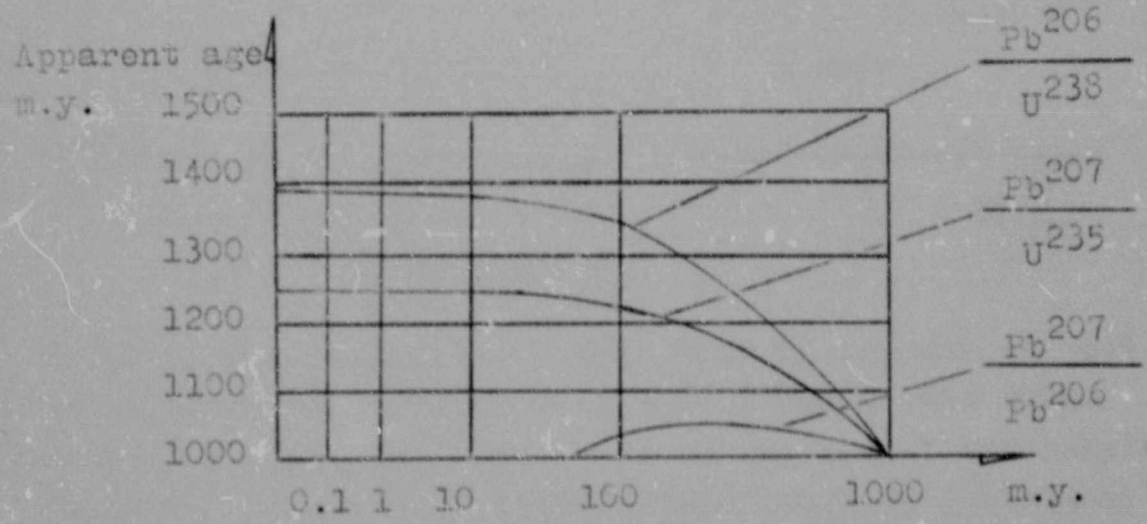


Figure 2: Effect on apparent ages for leaching of 30% of uranium at various times from a 1000 m.y. old mineral

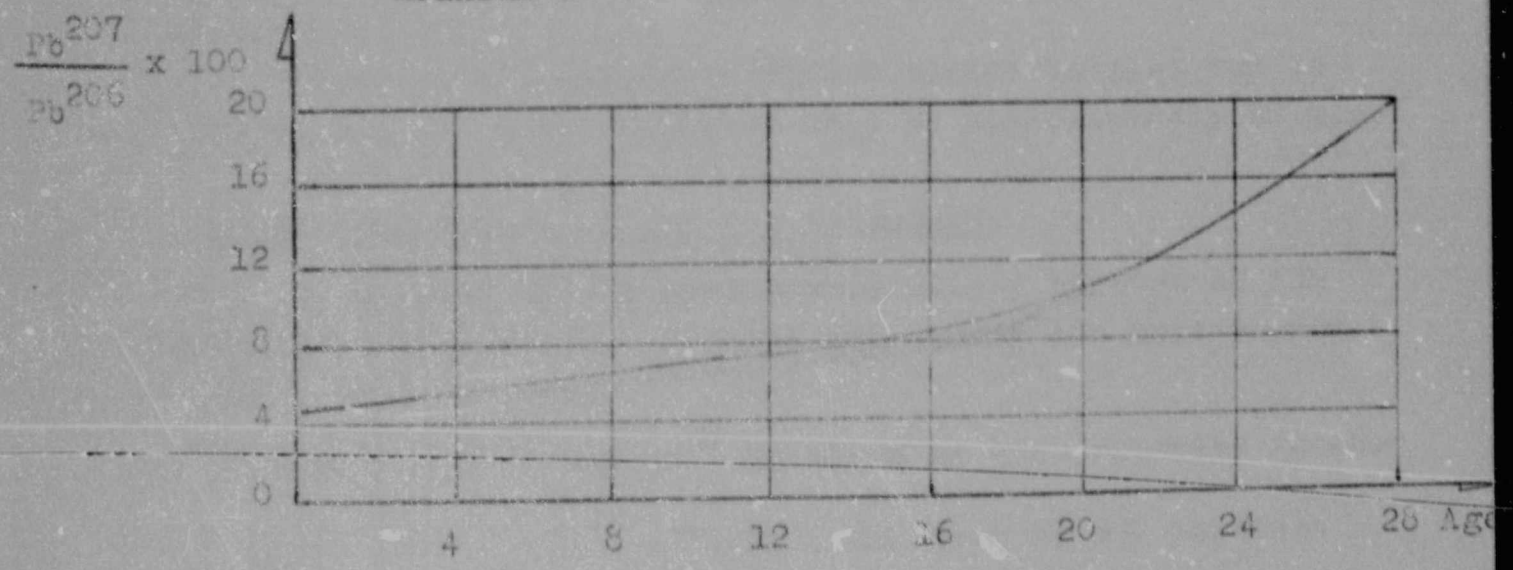
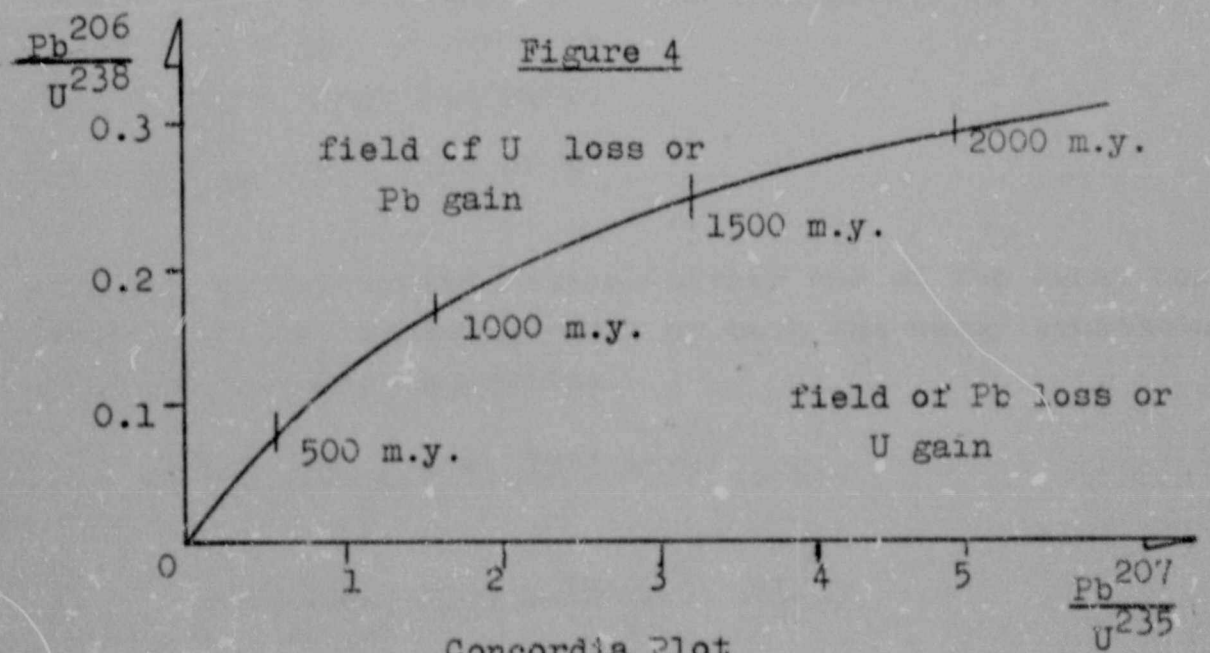


Figure 3: Variation of the $\frac{Pb^{207}}{Pb^{206}}$ ratio with time

The analysis of discordant ages was improved considerably by Wetherill in 1956 when he introduced the use of the "Concordia" curve. The "Concordia" is the locus of all the points having concordant $Pb^{207} - U^{235}$ and $Pb^{206} - U^{238}$ ages.

Figure 4



Concordia Plot

It was found (Wetherill, 1956) that an episode of lead loss would cause the samples to lie on a chord that cuts the curve at a point representative of the age of the sample.

Continuous solid diffusion (Nicolaysen, 1957) could also be responsible for Pb loss and it would have the same effect on the position of the sample on a corcordia plot as an episodic loss.

Silver (1963) has shown that a concordia plot can be used to resolve ages separated only by approximately 60 m.y.

A brief description of the K - Ar method:

This is the most widely used method mainly because of its relative simplicity and because K is among the most common rock-forming elements.

K^{40} decays to Ca^{40} and Ar^{40} as shown in the following scheme:

K^{40} → Ca^{40} (89.05%), emission of a β^- particle

K^{40} → Ar^{40} (10.95%), electron capture and emission of a γ ray at 1.46 MeV

If $\lambda\beta$ = probability that one K^{40} nuclide decays to a Ca^{40} nuclide in unit time

and λk = probability that a K^{40} nuclide decays to an Ar^{40} nuclide in unit time

then $R = \frac{\lambda k}{\lambda \beta}$ = branching ratio

and $\frac{.693}{\lambda k + \lambda \beta}$ = half life of K^{40}

Ages can be calculated knowing either one of the decay constants and the branching ratio or both the decay constants. From the following equations:

$$Ar^{40} = \frac{R}{1 + R} K^{40}(e^{\lambda\beta(1 + R)t} - 1)$$

OR:
$$t = \frac{1}{\lambda k + \lambda \beta} \cdot \ln(1 + \frac{\lambda k + \lambda \beta}{\lambda k} \cdot \frac{Ar^{40}}{K^{40}})$$

where: t = age

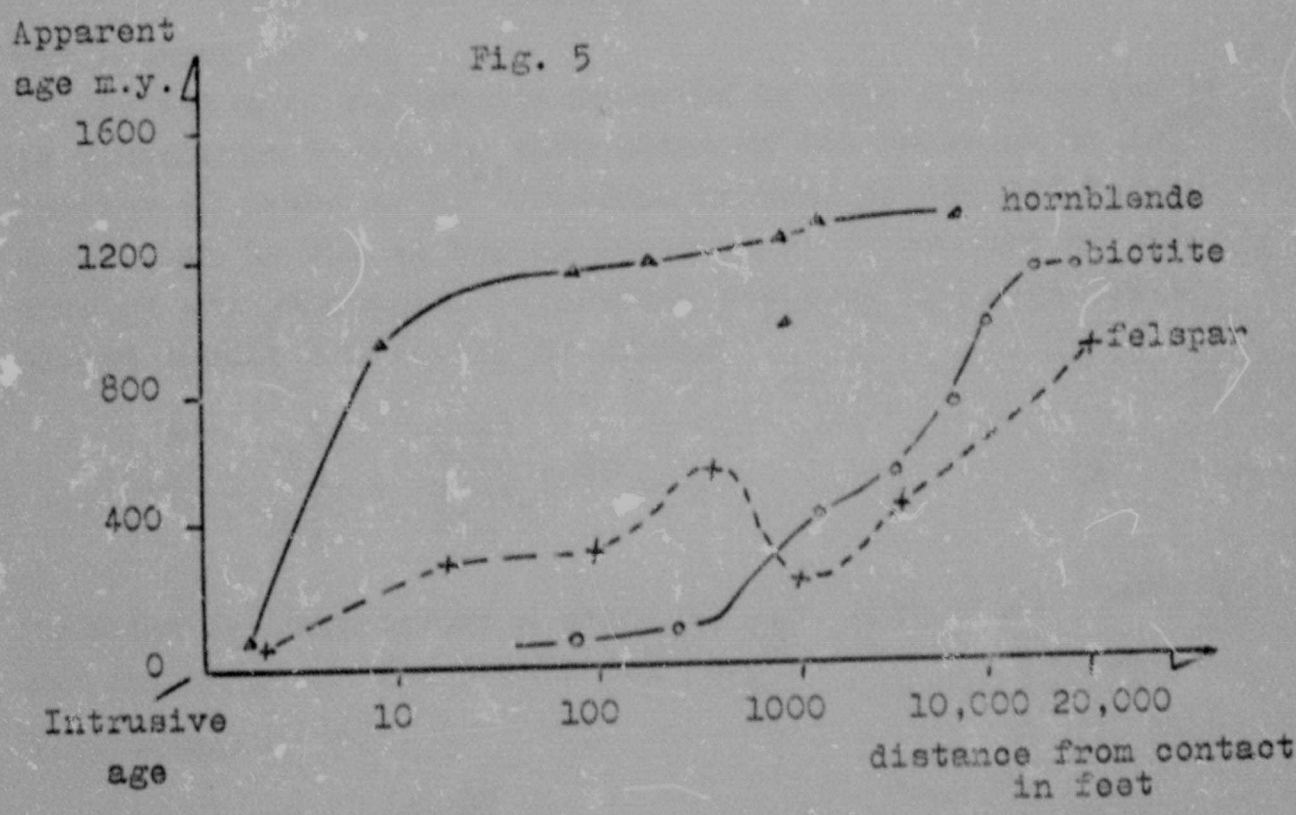
A major limitation of the K - Ar dating method is the leakage of Ar^{40}. This has been demonstrated on a number of occasions (e.g. McDougall et al., 1963; Hart, 1964; Aldrich et al., 1965). From a study of an intrusive contact between a tertiary stock (monzonite, granodiorite and syenodiorite) in a pre-cambrian gneiss, Hart (1964) has shown the variation of apparent age due to Ar^{40} loss for different minerals at different temperatures.

From fig. 5 (see over the page) it appears that hornblende has the best retentivity of argon and hornblende ages approximate to the real age of crystallisation; K felspar shows an erratic behaviour, and felspar ages are considered unreliable; biotite ages seem to be the most affected by argon loss and their ages frequently determine a period of metamorphism.

Hart and Dodd (1962) found that pyroxene has the peculiar quality of incorporating excess Ar, possibly in cavities or irregularities of the crystals. This makes pyroxene ages unreliable especially for rocks that have been deeply buried and/or thermally metamorphosed. On the

other hand this quality of the pyroxene is probably very useful when calculating total rock ages. McDougall (1966, p. 289) reports that K - Ar total rock ages can yield meaningful ages for fine-grained, holocrystalline, fresh rocks, and for rocks containing glass which is not devitrified. It is possible that total rock ages can be more accurate than separated mineral ages if the Ar freed by diffusion from one mineral can be retained from other minerals, for example pyroxene.

Fig. 5



The Rb - Sr Method:

The nuclide Rb^{87} decays to Sr^{87} by emission of a β particle with a half life of approximately 5.00×10^{10} years, determined by comparison of Rb - Sr and concordant U - Pb ages (Aldrich et al, 1956; Aldrich & Wetherill, 1958). The half life of Rb^{87} has also been estimated by physical determination of the decay constant, using different techniques, by a number of workers who have found significantly different values for it (Hamilton, 1965 pp. 86 - 88).

Applying the general law of transformation $N_t = N_o e^{-\lambda t}$, the decay of Rb^{87} to Sr^{87} can be expressed

by the equation:

$$Sr_t^{87} = Sr_o^{87} + Rb_t^{87} (e^{\lambda t} - 1)$$

substituting $N_t = Rb_t^{87}$ (present day no. of atoms of Rb^{87})
and $N_o = Rb_t^{87} + (Sr_t^{87} - Sr_o^{87})$ (Sr_t^{87} is the present day no. of atoms of Sr^{87}, and Sr_o^{87} is the no. of atoms of Sr^{87} present at the time of the last isotopic homogenization),
and solving for Sr_t^{87}.

As isotopic ratios are measured by mass spectrometry it is convenient to divide both sides of the equation by Sr_t^{86} (number of atoms of Sr^{86} nuclide present in the sample today, equal to the number of atoms of Sr^{86} present at the time of homogenization - provided the rock has remained a closed chemical system), obtaining:

$$\frac{Sr_t^{87}}{Sr_t^{86}} = \frac{Sr_o^{87}}{Sr_o^{86}} + \frac{Rb_t^{87}}{Sr_t^{86}} (e^{\lambda t} - 1) \qquad (i)$$

Equation (i) represents a straight line with slope $(e^{\lambda t} - 1)$ and intercept on the y-axis Sr_o^{87}/Sr_o^{86}.

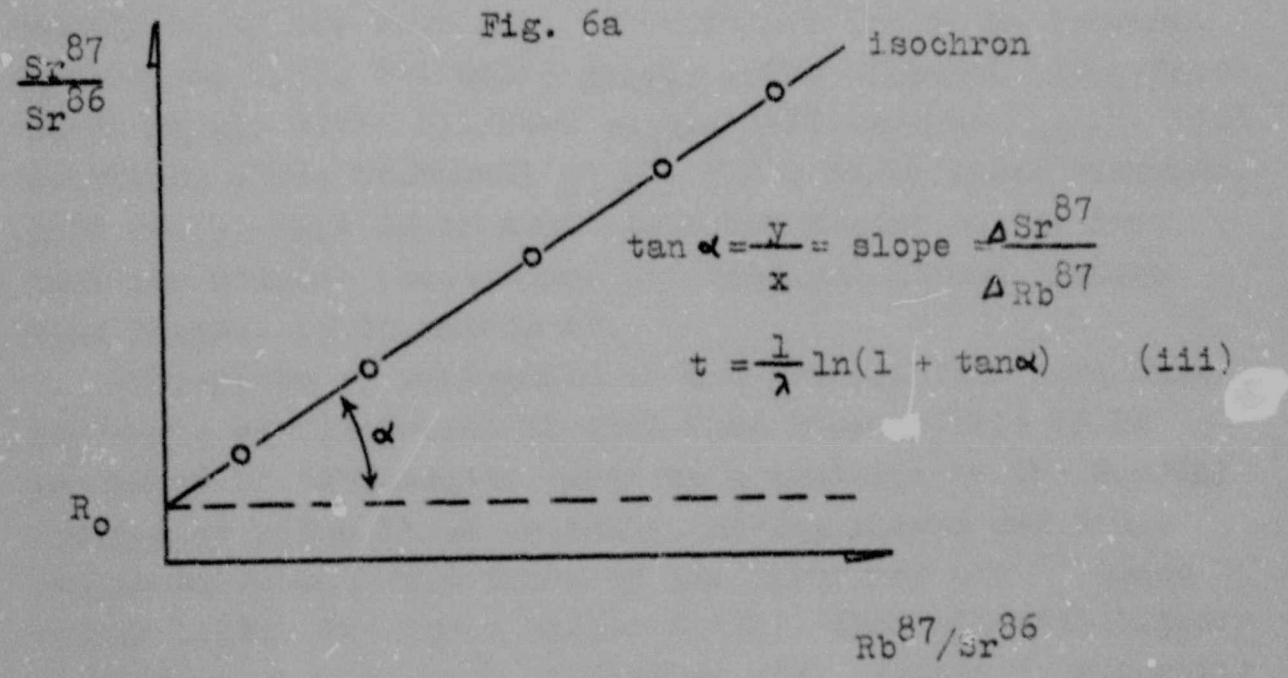
From equation (i)

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{\Delta Sr^{87}}{Rb_t^{87}}\right) \qquad (ii)$$

where $\Delta Sr^{87} = Sr_t^{87} - Sr_o^{87}$ = radiogenic Sr^{87}, and (ii) can be used to calculate the age t of a sample if the initial Sr_o^{87} is known. The age and the Sr_o^{87} can be found by (i) from a suite of samples of the same age and same initial ratio Sr_o^{87}/Sr_o^{86}. If the samples have remained closed chemical systems since crystallisation, the ratios Rb_t^{87}/Sr_t^{86}, Sr_t^{87}/Sr_t^{86} for each sample will be solution of (i) and will lie on a straight line that has an intercept on the y-axis equal to the initial ratio $R_o = Sr_o^{87}/Sr_o^{86}$ and a slope proportional to the age of crystallisation.

Such a line is called an isochron, and using the method of least squares, one can calculate the slope and intercept, proportional respectively to $t_{\lambda}^{(approx)}$ and R_o. Graphic representation of an isochron can be seen in fig.6a (after Nicolaysen 1961).

Fig. 6a



The isochron method, sometimes called "the B.P.I. method", is at present commonly used in Rb - Sr work and since this is the method used in the present investigation, the description of Rb - Sr methods will be limited to it and its applications.

If a mineral phase has undergone loss or gain of either parent or daughter nuclides it follows that the sample will not lie on the isochron and the apparent age will vary accordingly. See fig.6b

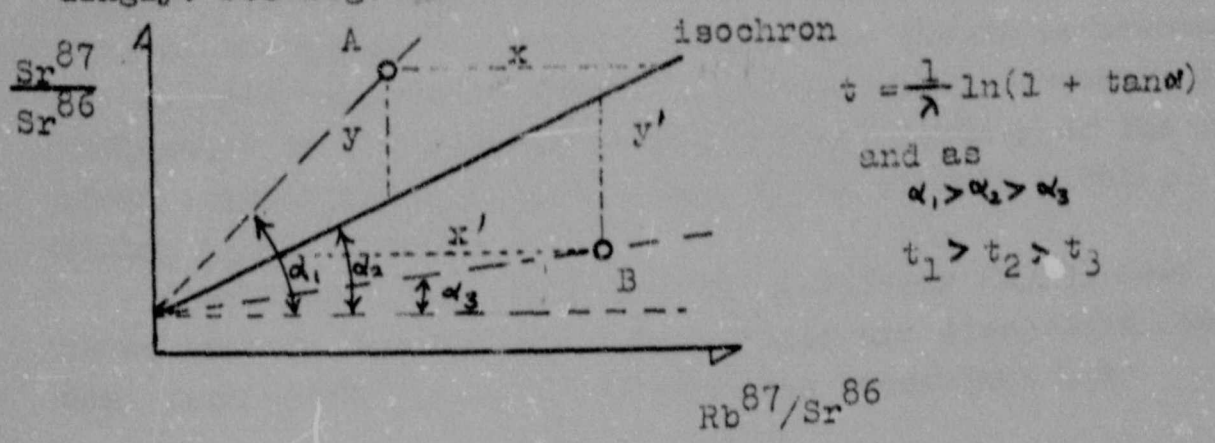


Fig. 6b

Sample A can either have lost Rb^{87} or gained Sr^{87} and the segments x and y are proportional respectively to the Rb lost or the Sr gained. Conversely, for the point B, y' is proportional to the lost Sr, x' to the gained Rb.

Separated minerals from a rock suite, which must necessarily be of the same age, often do not lie on an isochron (Schreiner 1958; Fairbairn et al., 1960; Allsopp, 1961; Fairbairn et al, 1961; Clifford et al, 1962; Lanphere et al, 1963 Moorbath, 1963; McDougall et al, 1963; Hart, 1964; Richards, 1966 etc.). This is in most cases attributed to the fact that the mineral phases have not remained closed systems with respect to Rb and/or Sr.

Movements of radiogenic Sr are probably the more common cause of discordant mineral ages because this Sr is generated by radioactive decay at a position in the crystal lattice at which it is unstable, having charge and ionic radius different from those of the parent Rb (Sr^{++} ionic radius 1.18A; Rb^{+} ionic radius 1.47A). Minerals with higher Rb content like biotite, K-felspar etc. (except in muscovite that has a high retentivity), are more liable to lose Sr^{87} and therefore to give low ages (see point B, fig.6b). Sometimes minerals like plagioclases with small Rb content, trap the radiogenic Sr freed from other minerals, and give very high ages (see point A, fig.6b).

Hurley et al (1963) have suggested that at depth a period of cooling of an igneous rock can be as long as 200 m.y. They have estimated that for a good portion of this period the temperature could be high enough to promote Sr^{87} diffusion. Mineral ages that are lower by one or two hundred million years can plausibly be ascribed to the cooling history of the rock, but wider discordances cannot be accounted for in this way. It is commonly accepted that movements of radiogenic Sr are related to the thermal history of the rock after crystallisation as has been shown by Hart (1964), Hurley et al (1963) etc.

Schreiner (1958) and Compston & Jeffrey (1959) have shown that in cases where mineral ages are discordant, measurement from total rock samples can give concordant ages.