

FISSION XENON DATING

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by

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A Thesis

Submitted to the School of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

June 1975

DOCTOR OF PHILOSOPHY (1975)  
(Physics)

McMASTER UNIVERSITY  
Hamilton, Ontario

TITLE: Fission Xenon Dating

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NUMBER OF PAGES: (xi) 97

## ABSTRACT

A new dating method has been developed which uses fission product xenon in a manner similar to radiogenic argon in the  $^{40}\text{Ar} - ^{39}\text{Ar}$  method. Measurable quantities of spontaneous fission xenon accumulate with time in rocks and minerals containing approximately 1 ppm or more of uranium as a result of the spontaneous fission of  $^{238}\text{U}$ . In the past, attempts have been made to date this type of sample by measuring the absolute amount of fission product xenon and the uranium content. In the new method a sample is irradiated in a thermal neutron flux to implant xenon from the neutron induced fission of  $^{235}\text{U}$  in amounts proportional to the uranium content. After a short cooling period (before radioactive  $^{133}\text{Xe}$  has decayed) the sample is placed in a high vacuum system and the xenon is released by heating in a series of temperature steps. For each step the isotopic composition of the xenon is measured using a high sensitivity mass spectrometer and the ratio of spontaneous fission xenon to neutron fission xenon is calculated. Fission xenon ages for all steps are then calculated from the spontaneous

to neutron fission xenon ratios and the measured integrated neutron flux.

The method has several advantages over the conventional U - Xe technique. (a) The measurement of isotope ratios is inherently more precise than the measurement of absolute quantities. (b) Whereas the conventional U - Xe technique measures the sample date only once, the method described in this thesis measures the sample date several times. (c) If a geological disturbance has caused loss of fission xenon a valid date can still be obtained using the low mobility xenon released at high temperatures. (d) In some samples disturbed dates as well as initial formation dates can be measured.

The method was developed and evaluated by a series of experiments which dated four zircon samples, one sphene sample, and a carbonatite sample. The zircon and sphene samples had been dated in other laboratories by the conventional U - Th - Pb and Rb - Sr methods. Fission xenon dating of these samples provided valuable new geochronological information. The experiments also showed that in addition to the advantages mentioned, the new method appears to be better able to see past metamorphic events than other methods.

## ACKNOWLEDGEMENTS

I thank Dr. W. B. Clarke for his patience, advice, and inspiration over the past years. I also thank Dr. W. J. Jenkins, Mr. J. E. McFee, Mr. M. W. Davis, Mr. C. E. McEwing and Dr. A. Robertson for many interesting discussions, Dr. H. P. Schwarcz and Dr. J. H. Crocket for helpful advice, and Dr. T. J. Kennett, Dr. K. Fritze, and Dr. J. W. Harvey for valuable suggestions.

I am indebted to Dr. C. J. Allègre, Dr. S. R. Hart, Dr. D. York and Dr. V. R. Murthy for providing the samples. Special thanks are due to Mr. E. M. Beaver for technical advice and assistance, Mrs. Dorothy Matthews for the difficult task of typing the manuscript, and Mr. D. S. Hodgson for the artwork of the illustrations.

Above all I wish to express my gratefulness to my parents for their support and encouragement of all my endeavours. Also, I wish to express my appreciation to Mr. N. Veenhof who first stimulated my interest in science and Dr. R. E. Green who expertly guided my initial research efforts.

This work was made possible by grants from the National Research Council of Canada and assistantships and scholarships from the government of Ontario and McMaster University.

## TABLE OF CONTENTS

CHAPTER		PAGE
1	INTRODUCTION	1
2	THE AGE EQUATION	6
3	EXPERIMENTAL	
	Techniques and Numerical Treatment of the Data.	10
	A. Samples and Sample Preparation	10
	1. Air Samples	10
	2. Rock Samples	10
	3. Rock Samples - Irradiated	11
	4. Zircons and Spheue - Irradiated	11
	B. Extraction	12
	1. The Extraction Line	12
	2. Single Heating Step Extractions	14
	3. Stepwise Heating Experiments	15
	C. Mass Spectrometry	16
	1. The Mass Spectrometer	16
	2. Isotopic Abundance Measurements	17
	3. Calibration (Mass Discrimination and Sample Size)	18
	D. Flux Measurements	18
	1. Flux Monitor Gamma Ray Counting	18
	2. Integrated Neutron Flux Measurements	19
	E. Calculation of the Fission Xenon Ages	20
	1. Dates Calculated from Paired Isotopes	20
	2. Least Squares Fit Dates	21
	3. Complications Affecting the Determination of Fission Xenon Dates	25

TABLE OF CONTENTS

CHAPTER		PAGE
3	F. Neutron Fission Yield Corrections	28
	1. Decay Corrections to the Yields $Y_N^{133}$ , $Y_N^{132}$ , and $Y_N^{131}$	28
	2. The $^{135}\text{Xe}(n,\gamma)^{136}\text{Xe}$ Correction to the Yield $Y_n^{136}$	29
	G. Whole Sample Isotopic Abundances	29
4	RESULTS	31
	A. Unirradiated Samples	31
	B. Zircons and Sphene Dates	34
	1. Sample List	34
	2. Sphene Sample L - 6	34
	3. Zircon Sample M 4082	41
	4. Zircon Sample K 710	45
	5. Charnockite Zircon Sample	47
	6. Zircon Sample G 2	51
	C. Normal Rock Sample Dates	54
5.	DISCUSSION	59
	A. General Interpretation of the Zircon Data	59
	B. The Western Ahaggar Samples M 4082 and L - 6	62



## TABLE OF CONTENTS

CHAPTER		PAGE
5	C. The Eastern Pyrenees Sample Charnockite and G 2	67
	D. Normal Rock Samples	71
	E. Miscellaneous	75
	1. Calibration by a Standard of Known Age	75
	2. Optimization of the Irradiation Time	75
6	CONCLUSION	77
APPENDIX		
I	Flux Depression Correction (Cylindrical Samples)	80
II	The Decay Equations and the Decay Chains for Masses 131, 132 and 133	82
III	The $^{135}\text{Xe}(n,\gamma)^{136}\text{Xe}$ Correction to $Y_N^{136}$	87
IV	Least Squares Analysis of an Isotopic Composition	89
	BIBLIOGRAPHY	93

LIST OF TABLES

TABLE		PAGE
1	Values Used in the Calculation of Fission Xenon Ages	24
2	Isotopic Composition of Unirradiated Samples	32
3	Zircon Samples	35
4	Fission Xenon Age of Sample L - 6	37
5	Fission Xenon Dates : Sample M 4082	42
6	Fission Xenon Dates : Sample K - 710	46
7	Fission Xenon Dates : Charnockite Sample	49
8	Fission Xenon Dates : Sample G 2	52
9	Fission Xenon Dates : Sample KA 64 - 2	55

## LIST OF FIGURES

FIGURE		PAGE
1 (a)	Quartz Irradiation Vial (Large Sample)	13
1 (b)	Quartz Irradiation Vial (Zircons)	13
2	The Extraction Line	13
3	Relative Isotopic Abundance Error as a Function of Absolute Abundance	40
4	The Fission Xenon Dates of Sample M 4082 Versus the Cumulative Amount of Fission $^{136}\text{Xe}$ Released	44
5	The Fission Xenon Dates of Sample K 710 Versus the Cumulative Amount of Fission $^{136}\text{Xe}$ Released	48
6	The Fission Xenon Dates of the Charnockite Sample Versus the Cumulative Amount of Fission $^{136}\text{Xe}$ Released	50
7	The Fission Xenon Dates of Sample G 2 Versus the Cumulative Amount of Fission $^{136}\text{Xe}$ Released	53
8	The Correlation of Neutron Fission Product Xenon and Spontaneous Fission Product Xenon from Sample KA 64 - 2	56

## LIST OF FIGURES

FIGURE		PAGE
9	The Fission Xenon Dates of Sample KA64 - 2 Versus the Cumulative Amount of Fission $^{136}\text{Xe}$ Released	57
10	The Western Ahaggar Region	63
11	The Canigou and Agly Massifs in the Eastern Pyrenees	68
12	The Relative Spontaneous Fission Product Xenon Abundance of Normal Uranium Content Samples	73

CHAPTER 1  
INTRODUCTION

Since the discovery by Becquerel of radioactivity (Becquerel, 1896) and a suggestion by Rutherford that the quantity of helium produced by the alpha decay of uranium and its daughters could be used to determine the age of terrestrial rocks (Rutherford, 1906), a variety of radioactive dating methods have been developed (see Faul, 1966, or York and Farquhar, 1972). When studying a particular sample or samples from a limited geographical area any one of these methods may be found to be deficient in some way. In fact, the geochronology of a region is usually determined by a combination of radioactive dating methods and even then some uncertainties may be left unresolved. Thus, provided a new method can supply extra information and is not too difficult experimentally, it can prove to be a valuable addition to existing dating techniques.

One of the many possible techniques which has received periodic attention (Butler et al. 1963; Schukoljukov and Mirkina, 1963) measures the amount of fission product xenon which has accumulated from the spontaneous fission of  $^{238}\text{U}$  and the uranium content of a sample. This information

when inserted into the U-Xe age equation (equation 5, p. 7) yields the age of the sample.<sup>†</sup>

This thesis presents this basic method with an innovation similar to one of Merrihue's inventions as a possibly powerful new technique of geochronology. Merrihue (1965), and Merrihue and Turner (1966) developed a variation of the K-Ar method, the  $^{40}\text{Ar} - ^{39}\text{Ar}$  method. Rather than measuring the potassium content directly samples were irradiated along with a flux monitor (a sample of known age) in a fast neutron flux in order to convert some of the potassium to argon by means of the reaction  $^{39}\text{K}(n,p)^{39}\text{Ar}$  so that the ages of the samples could be determined from the  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio. The precision of the  $^{40}\text{Ar} - ^{39}\text{Ar}$  technique proved to be inherently better than that of the K-Ar method except for samples with low K/Ca ratios and younger than  $10^8$  years (Dalrymple and Lanphere, 1971).

In addition to the advantages of precision and simplicity the  $^{40}\text{Ar} - ^{39}\text{Ar}$  technique has the advantage that argon can be released from a sample by heating the sample in

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<sup>†</sup>For samples less than 500 million years old the age is proportional to the amount of fission xenon in the sample divided by the amount of uranium in the sample.

a series of steps of increasing temperature. Thus when one or more geological events have disturbed a sample since its initial formation the dates of these disturbances can sometimes be determined from  $^{40}\text{Ar}/^{39}\text{Ar}$  ratios measured in argon released at lower temperatures (Turner et al., 1966).

The U - Xe technique can be modified in a similar manner (Teitsma et al., 1974 and 1975) gaining for the new method, the fission xenon dating method, the same advantages which resulted from modifying the K - Ar technique. The modification is made possible by the following circumstances:

1. Although other naturally occurring nuclei fission spontaneously, either their spontaneous fission half lives are too long or their abundances are too small to detect sufficient quantities of fission products from these nuclei, either for use in a radioactive dating method or as a possible source of interference with fission products resulting from the spontaneous fission of  $^{238}\text{U}$ .

2. When a sample is irradiated in a thermal neutron flux the only nucleus which can be induced to fission is  $^{235}\text{U}$  since the fissioning of both  $^{238}\text{U}$  and  $^{232}\text{Th}$  require fast neutrons (Goldberg et al., 1966).

3. The ratio  $^{235}\text{U}/^{238}\text{U}$  is constant in natural uranium of terrestrial origin (Hamer and Robbins, 1960).

4. The isotopic composition of xenon produced by the neutron induced fission of  $^{235}\text{U}$  is distinctly different from that produced by the spontaneous fission xenon of  $^{238}\text{U}$  (see table 1).

There are a few exceptions to conditions 1. and 3. but these exceptions occur so rarely that they can be ignored.

Thus, irradiating a sample with thermal neutrons converts some of the uranium to xenon. Isotopic analysis of the xenon extracted from the sample after irradiation determines the ratio of spontaneous fissions to neutron fissions. Since this ratio is proportional to the ratio of the number of spontaneous fissions to the amount of  $^{238}\text{U}$  in the sample it is a measure of the age of the sample. A precise date is calculated by inserting the ratio plus the measured value of the integrated neutron flux into the fission xenon age equation (equation 9, p. 9 ).

The most important of the advantages of the fission xenon dating technique is the ability to use the method in conjunction with stepwise heating experiments, and the consequent possibility of measuring disturbed ages as well as an initial age. In this type of experiment, fission xenon dating has a further advantage resulting from the



ability to use up to six fission xenon isotopes: the assumption that the neutron fission xenon is implanted in sites similar to those in which the spontaneous fission xenon is implanted, can be examined at each temperature step by the agreement among the results from several pairs of isotopes. In comparison, the only check on the equivalent assumption in  $^{40}\text{Ar} - ^{39}\text{Ar}$  stepwise heating experiments is how well the  $^{40}\text{Ar}$  release is correlated with the release of  $^{39}\text{Ar}$ .

The fission xenon dating technique is obviously suitable for samples which contain moderately high amounts of uranium. However in order to increase the applicability and hence usefulness of the method, its development was aimed at dating samples of normal U content ( $\sim 1$  p.p.m.) as well as samples of high U content. The remainder of the thesis, beginning with the derivation of the age equation, describes this development both theoretical and experimental and the results obtained from a variety of samples.

CHAPTER 2  
THE AGE EQUATION

$^{238}\text{U}$  is an unstable nucleus with two known modes of decay, alpha particle emission and spontaneous fission. While the dating method formulated in this thesis depends on detecting fission product xenon accumulated from the fission decay mode, the  $^{238}\text{U}$  half life is determined by the alpha decay mode since alpha particle emission occurs much more frequently than spontaneous fission. Thus the amount of  $^{238}\text{U}$  present at any time,  $t$ , is

$$^{238}\text{U} = ^{238}\text{U}_0 e^{-\lambda_\alpha t} \quad (1)$$

where

$^{238}\text{U}_0$  = number of atoms of  $^{238}\text{U}$  present at time  $t=0$

$\lambda_\alpha$  = alpha decay constant

and the spontaneous fission rate at any time,  $t$ , is

$$\begin{aligned} \frac{dS}{dt} &= \lambda_S ^{238}\text{U} \\ &= \lambda_S ^{238}\text{U}_0 e^{-\lambda_\alpha t} \end{aligned} \quad (2)$$

By integrating this last equation, and by substituting for  $^{238}\text{U}_0$  from equation 1, it follows that the total number of fissions detectable after a lapse of time,  $T$ , assuming the record has not been altered is

$$S = \frac{\lambda_S}{\lambda_\alpha} \quad ^{238}\text{U} (e^{\lambda_\alpha T} - 1) \quad (3)$$

where  $S$  = total number of fissions

$^{238}\text{U}$  = number of atoms of  $^{238}\text{U}$  present at time  $T$

$\lambda_S$  = spontaneous fission decay constant

The isotopes of xenon produced as a result of the fission process are thus present in amounts given by relations of the form

$$i_{\text{Xe}_S} = Y_S^i S \quad (4)$$

which become upon substitution from equation (3)

$$i_{\text{Xe}_S} = Y_S^i \quad ^{238}\text{U} \frac{\lambda_S}{\lambda_\alpha} (e^{\lambda_\alpha T} - 1) \quad (5)$$

where  $i_{\text{Xe}_S}$  = number of atoms of  $i_{\text{Xe}}$  accumulated from the fission process

$Y_S^i$  = spontaneous fission chain yield for mass  $i$ .

Equation (5) is the U - Xe age equation. In deriving it explicit use was made of the assumption that no significant amount of fission xenon is lost between the time of the rock formation and the present. A better approach relaxes this assumption.

The number of fissions which occur in a sample irradiated in a thermal neutron flux as a result of the neutron induced fission of  $^{235}\text{U}$  is given by the equation

$$N = \sigma_{235} \phi t \text{ } ^{235}\text{U} \quad (6)$$

where  $\sigma_{235}$  = thermal neutron fission cross section of  $^{235}\text{U}$

$\phi t$  = integrated thermal neutron flux

$^{235}\text{U}$  = number of  $^{235}\text{U}$  atoms in the sample

As in the case of spontaneous fission, among the products of neutron induced fission are several isotopes of xenon so that after irradiation, these are present in amounts given by equations of the form

$${}^i\text{Xe}_N = y_N^i N \quad (7)$$

where  ${}^i\text{Xe}_N$  = number of atoms of  ${}^i\text{Xe}$  accumulated from the neutron fission process

$y_N^i$  = neutron fission yield of isotope  $i$  .

Taking the ratio of equations 3 and 6, the ratio of spontaneous fissions to neutron fissions is

$$S/N = \left( \frac{238_U}{235_U} \right) \frac{\lambda_S}{\lambda_\alpha} \frac{(e^{\lambda_\alpha T} - 1)}{\sigma_{235} (\phi t)} \quad (8)$$

Rearrangement of this relation expresses the age equation in the more useful form

$$T = \frac{1}{\lambda_\alpha} \ln \left[ 1 + \left( \frac{235_U}{238_U} \right) \frac{\lambda_\alpha}{\lambda_S} \left( \frac{S}{N} \right) \sigma_{235} (\phi t) \right] \quad (9)$$

where, provided well thermalized neutrons<sup>†</sup> are used,  $\phi t$ , the integrated neutron flux, is easily measured using a flux monitor (e.g. 1% Co - Al) and where as a consequence of equations 4 and 7 the ratio, S/N, can be determined from measurements of the ratio of spontaneous fission xenon to neutron fission xenon.

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<sup>†</sup> The ratio of the activity induced in cobalt to that produced in cobalt wrapped in cadmium should be  $\gtrsim 15$ .

## CHAPTER 3

### EXPERIMENTAL

#### Techniques and Numerical Treatment of the Data

#### A. Samples and Sample Preparation.

##### 1. Air Samples

Samples of xenon prepared from air were used to calibrate the mass spectrometer. The air samples were prepared by drawing out long capillary tubes from pieces of 6 mm. OD pyrex tubing. A section of capillary tubing which appeared uniform in diameter was filled with mercury and the length of mercury drawn into the capillary was measured. Subsequent weighing of the mercury determined the volume per unit length of the tubing ( $\sim 0.8 \times 10^{-3}$  ml/cm.). The capillary tubing was sealed off and sectioned into air samples containing  $\sim 3 \times 10^{-3}$  cc. STP of air by local melting of the glass.

##### 2. Rock Samples

Since the initial aim was to use the fission xenon dating method to date rocks containing 1 ppm or more of uranium, a variety of terrestrial rocks were examined for excess spontaneous fission xenon. A number of the samples had already been crushed and sieved. These were used without further crushing or sorting. A new crusher was machined for the remaining samples to minimize possible sources of contamination. After

a sample had been crushed the crusher was cleaned with fine emery paper and running water and was dried before the next sample was crushed. Sieves were used to sort the crushed samples into a 24 - 48 mesh fraction, and a < 48 mesh fraction. All particles from a previous sample were removed from the sieves before the next sample was sieved. Only the 24 - 48 mesh fractions were used in the experiments.

### 3. Rock Samples - Irradiated

Samples from three rock specimens were irradiated. One gram quantities of each were placed in evacuated quartz vials (see figure 1a). Two 1% Co-Al wires were taped to opposite sides of each vial. In addition, a 1% Co-Al wire was placed in the centre of each sample. These wires, cut to match the height of the samples in the vials, were used to monitor the neutron flux during the irradiations. The activities of the two outside wires were averaged, thus correcting for neutron flux asymmetry. The central wires were used to correct for neutron flux depression in the samples (see Appendix I for the flux depression calculation).

### 4. Zircons and Sphene - Irradiated

Four samples of zircon and one sample of sphene were chosen for irradiation and subsequent dating because these minerals have a high uranium content and are fairly retentive for radiogenic helium (Hurley 1954). Since these samples were

small ( $\sim 20$  mg.) they were wrapped in aluminum foil to facilitate handling. Each of the samples was irradiated alongside a single  $1\%$  Co-Al flux monitor in an evacuated quartz vial (see figure 1b).

## B. Extraction

### 1. The Extraction Line

The extraction line is shown schematically in figure 2. The line was divided into two sections. The first was used for extraction and initial purification, the second for final purification, for separating xenon from the other noble gases, and for admitting xenon into the mass spectrometer for isotopic analysis. The construction of the line was such that work could proceed simultaneously in both sections.

The resistance heating furnace capable of heating samples up to  $1400^{\circ}\text{C}$  consisted of a Kanthal REH tubular heating element surrounded by alumina powder insulation. The temperature inside the furnace was controlled and measured with a Bach-Simpson model 5626 indicating temperature controller which used a Pt -  $13\%$  RhPt thermocouple as a heat sensor.

Purification of the gas samples was accomplished by means of titanium getter pumps. During purification titanium sponge was slowly cooled from about  $800^{\circ}\text{C}$  to about  $100^{\circ}\text{C}$



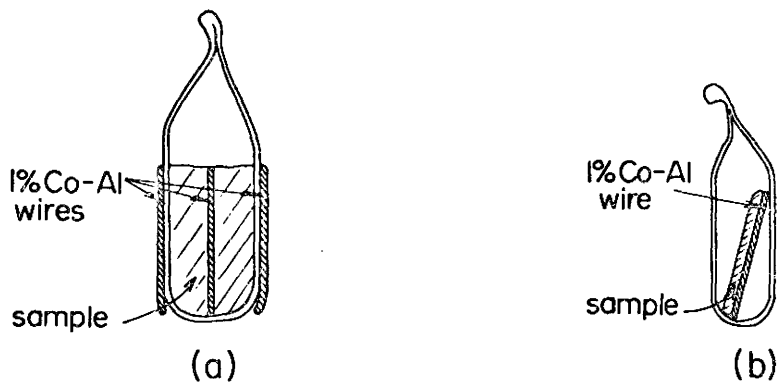


Figure 1 (a) Quartz Irradiation Vial (large sample)  
 (b) Quartz Irradiation Vial (Zircons)

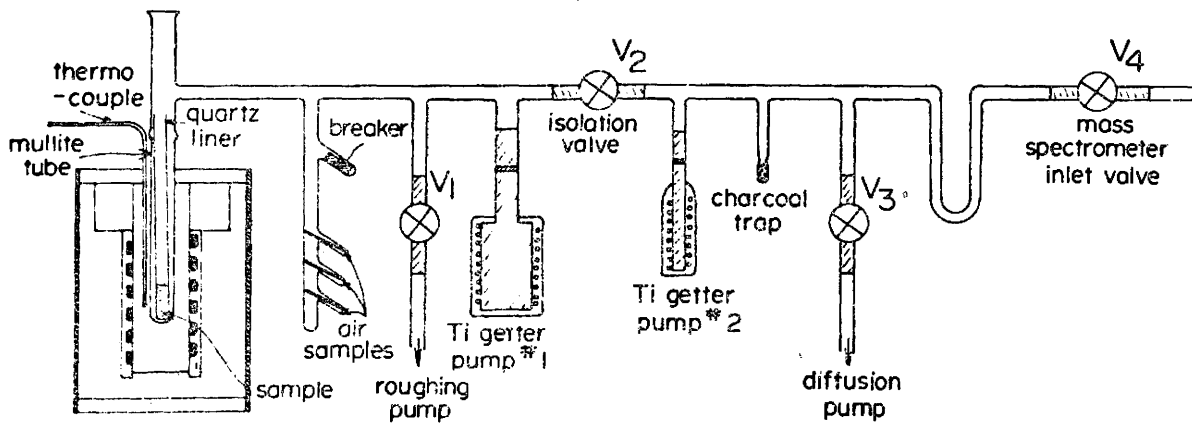


Figure 2 The Extraction Line

thus removing all but the noble gases.

Gas samples were transferred from the first to the second section by condensing on the charcoal trap while it was held at liquid nitrogen temperature ( $-186^{\circ}\text{C}$ ). Xenon was separated from the other rare gases by warming the charcoal trap to dry ice temperature ( $-80^{\circ}\text{C}$ ). At this temperature xenon was retained by the trap while other rare gases were released and pumped away.

The control valves,  $V_1$ ,  $V_2$ ,  $V_3$  and  $V_4$ , were stainless steel Nupro model SS-4BW-SW bellows valves. Valve  $V_1$  was kept closed except when pumping the line down from atmospheric pressure. Valve  $V_2$  isolated the two sections of the line from each other. Valve  $V_3$  opened to a high vacuum pump consisting of a liquid nitrogen trap in series with a mercury diffusion pump. Access to the mass spectrometer was controlled by valve  $V_4$ .

## 2. Single Heating Step Extractions

Xenon was released from the unirradiated rock samples and the sphene sample in a single heating step. A sample of either type from which xenon was to be extracted was put in a quartz liner positioned to place the sample in the centre of the resistance furnace. After the sample line had been evacuated the sample temperature was raised to  $200^{\circ}\text{C}$ . This temperature was maintained for one hour and the gases thus

evolved from the sample were pumped away. The sample line was then flamed to remove adsorbed gases, particularly xenon.

Next, the first section of the sample line was isolated by closing valve  $V_2$  and the furnace temperature was raised to  $1400^{\circ}\text{C}$ . After one hour at  $1400^{\circ}\text{C}$  the furnace was shut off and the gases evolved from the sample exposed to titanium at  $800^{\circ}\text{C}$ . The remaining gases were then transferred to the second section of the extraction line. The line was flamed briefly to ensure complete collection of the xenon. Upon completion of the transfer, the second section of the line was isolated by closing valves  $V_2$ ,  $V_3$ , and  $V_4$  and xenon was separated from the other rare gases which were pumped away by opening valve  $V_3$  for several minutes. The remaining gas sample was purified a second time and was then expanded into the mass spectrometer for isotopic analysis of the xenon.

### 3. Stepwise Heating Experiments

Xenon was extracted from the three irradiated rock samples and the four samples of zircon by heating from  $200^{\circ}\text{C}$  to  $1400^{\circ}\text{C}$  in a series of eight temperature steps. As in the single step heating experiments, gases evolved by heating the samples up to  $200^{\circ}\text{C}$  were discarded. The procedures for collecting, purifying and analyzing the xenon from each of the temperature

steps were the same as those described for the single step heating experiments.

## C. Mass Spectrometry

### 1. The Mass Spectrometer

The isotopic abundances were measured with a 90° sector, 10 inch radius, direction focusing mass spectrometer. The resolution of this instrument, 1 : 625, was sufficient to separate xenon from the isobaric hydrocarbons. Maximum sensitivity was achieved by machining the ion beam path from a solid block of inconel and by operating the mass spectrometer in the static mode. Under optimum conditions the spectrometer is capable of detecting approximately 5000 atoms of a rare gas isotope.

Samples were ionized and the resulting ions were accelerated by a Nier type ion source (Nier, 1947). The ion detector was a Johnston Laboratories MM-1 particle multiplier with a gain of  $\sim 10^5$ . The signal from the multiplier was amplified by a Cary model 401 vibrating reed amplifier and the output of the amplifier was recorded on a Hewlett-Packard model 680 strip chart recorder.

The pumping system consisted of a mercury diffusion pump and a Varian model 911 - 5021 ion pump connected to a pumping manifold by one inch Granville-Phillips ultra high

vacuum valves. The spectrometer could be isolated from the pumping manifold by a one inch valve of the same kind.

## 2. Isotopic Abundance Measurements

The raw data of an isotopic abundance measurement consisted of the peaks recorded by the strip chart as the magnetic field of the spectrometer was slowly varied. A measurement consisted of eight double scans over the desired mass range : masses 136 to 124 for the unirradiated samples and masses 136 to 129 for the samples which were dated. The height of each xenon peak was measured by ruler, and the times at which the peaks were recorded were read off the chart.

Due to the ion pumping action of the spectrometer during static analysis the sample was depleted rapidly in the course of a measurement ( $\sim$  one half the sample in 40 minutes). The resulting decrease as a function of time of the peak height of the isotope chosen for normalization was determined either graphically or by a polynomial least squares fit (see Bevington, 1969). The peak height of a second isotope recorded at a time  $t$ , was then divided by the peak height of the normalization isotope at time  $t$ , to determine the isotope ratio of the second isotope at time  $t$ .

Both depletion of the sample and memory from previous samples cause variation of the observed isotope ratios with

time. When feasible the ratios were extrapolated by a linear least squares fit to the time at which the sample was admitted to the mass spectrometer. When the variation was not linear the extrapolation was done by a polynomial fit. In the latter case the fit was checked by plotting.

### 3. Calibration (Mass Discrimination and Sample Size)

The extrapolated ratios were corrected for instrumental mass discrimination by adjusting the ratios so that the mean isotopic composition of the air samples was equal to the absolute isotopic composition of atmospheric xenon (see table 2) as determined by Nier (1950). Since the sizes of the air samples had been measured (see section A 1), the absolute abundance of the xenon extracted from a sample could be determined by peak height comparison.

The terms "isotopic composition", "isotopic abundance", and "isotopic ratio" when used in the remainder of the thesis, refer to the extrapolated ratios corrected for instrumental discrimination.

#### D. Flux Measurements

##### 1. Flux Monitor Gamma Ray Counting

The gamma ray activity of  $^{60}\text{Co}$  in each 1% Co - Al flux monitor was measured relative to a similarly shaped Co - Al standard of precisely known activity. To reduce the

interfering activity of  $^{24}\text{Na}$  ( $T_{1/2} = 15$  hours), formed in the reaction  $^{27}\text{Al}(n,\gamma)^{24}\text{Na}$ , to a negligible level, the activity of a flux monitor was not determined until at least ten days after an irradiation.

## 2. Integrated Neutron Flux Measurements

The cobalt content of a flux monitor was determined by weighing the monitor. The integrated neutron flux,  $\phi t$ , was then calculated by inserting the activity of the monitor and its cobalt content into the expression

$$\phi t = \frac{\text{activity}}{N_{\text{Co}} \sigma_{\text{Co}} \lambda_{\text{Co}}}$$

where  $N_{\text{Co}}$  = number of atoms of  $^{59}\text{Co}$

$\sigma_{\text{Co}}$  = neutron capture cross section of  $^{59}\text{Co}$

$\lambda_{\text{Co}}$  = decay constant of  $^{60}\text{Co}$ .

The value of the cobalt cross section, 39.2 barns, used in the above calculations included a small correction for epithermal neutron capture (Westcott, 1962). This value was based on a 2200 m/sec cross section of 37.3 barns which compares favourably with a recent measurement of  $37.15 \pm 0.08$  barns (Dilg, 1973). The errors in the flux measurements are estimated to be less than 1.5%.

## F. Calculation of the Fission Xenon Ages

### 1. Dates Calculated from Paired Isotopes

Of the two methods available for determining the fission xenon ages of irradiated samples, the most straightforward is to calculate a set of fission xenon dates from all possible pairs of fission xenon isotopes. In this method, the isotopes  $^{129}\text{Xe}$  and  $^{130}\text{Xe}$  which are not produced in significant quantities in the fission process are used to determine the size of the atmospheric component in a measured isotopic composition by calculating the best estimate of the  $^{129}\text{Xe}$  isotope ratio relative to the normalization isotope. This ratio times the isotopic composition of atmospheric xenon as given in table 2 (i.e. with  $^{129}\text{Xe} \equiv 1.000$ ) is subtracted from the measured composition. The remaining, fission xenon isotopic composition, is then assumed for the purpose of the calculations to be due to xenon obtained from fission of  $^{238}\text{U}$  and  $^{235}\text{U}$  nuclei.

Expressing the amount of  $^i\text{Xe}$  (fission) as

$$^i\text{Xe (fission)} = N Y_N^i + S Y_S^i \quad (2)$$

where

$Y_N^i$  = absolute neutron fission yield of  $^i\text{Xe}$

$Y_S^i$  = absolute spontaneous fission yield of  $^i\text{Xe}$

$N$  is proportional to the number of neutron fissions

$S$  is proportional to the number of spontaneous fissions,



the fission xenon isotope ratio of a given pair of isotopes can be expressed as

$$\frac{{}^i\text{Xe (fission)}}{{}^j\text{Xe (fission)}} = R_{ij} = \frac{(N Y_N^i + S Y_S^i)}{(N Y_N^j + S Y_S^j)} \quad (3)$$

This equation when rearranged shows that the ratio of the number of neutron fissions to the number of spontaneous fissions as measured by this pair of isotopes is

$$\frac{S}{N} = \frac{(Y_N^i - R_{ij} Y_N^j)}{(R_{ij} Y_S^j - Y_S^i)} \quad (4)$$

In the present work five fission xenon isotopes were measured. Thus substituting the values of  $S/N$  obtained from all pairs of fission isotopes of a measured isotopic composition into the fission xenon age equation (equation (9) p. 9) resulted in ten dates, although it must be pointed out that the ten dates thus obtained represent only four independent age determinations.

## 2. Least Squares Fit Dates

Least squares analysis of the isotopic abundances is a second method for determining the fission xenon dates of a sample. Ideally, a measured isotopic composition is

the sum of three components, a neutron fission component, N, a spontaneous fission component, S, and an atmospheric component, A. Hence, letting  $Y_N^i$ ,  $Y_S^i$ , and  $Y_A^i$  be the yields of the components indicated by the subscripts, the isotopic abundance of isotope, i, is the sum

$${}^i\text{Xe} = Y_N^i N + Y_S^i S + Y_A^i A \quad (5)$$

Since  ${}^i\text{Xe}$  can not be measured exactly in practice there is a difference,

$$d_i = {}^i\text{Xe (measured)} - (Y_N^i N + Y_S^i S + Y_A^i A) \quad (6)$$

between the measured value of  ${}^i\text{Xe}$  and the exact value of the sum on the right hand side of equation 5. Squaring this deviation and adding on to it the squares of the deviations of all other measured isotope ratios forms the sum of the squares of the deviations,

$$M = \sum_i \left[ {}^i\text{Xe (measured)} - (Y_N^i N + Y_S^i S + Y_A^i A) \right]^2 \quad (7)$$

The method of least squares consists of minimizing this sum with respect to the components, N, S, and A (i.e. setting each of the partial derivatives,  $\frac{\partial M}{\partial N}$ ,  $\frac{\partial M}{\partial S}$ , and  $\frac{\partial M}{\partial A}$ , equal to zero). The three normal equations which result

from this procedure are then solved for the best estimate of the values of  $N$ ,  $S$ , and  $A$ . If in the above equation the absolute fission yields are used for the  $Y_N^i$  and the  $Y_S^i$  then the ratio,  $N/S$ , equals the number of neutron fissions divided by the numbers of spontaneous fissions and hence substituting this ratio into the fission xenon age equation (equation 9, p. 9) determines the fission xenon date.

Two methods for solving the normal equations for an arbitrary number of components are given in Appendix IV. In this appendix the symbol  $R_i$  is used in the place of  $^i\text{Xe}$  and for the sake of completeness the theory is developed for cases where the errors ( $\sigma_i$ ) or at least the relative weights  $\omega_i$  (proportional to  $1/\sigma_i^2$ ), of the isotope ratios are known.

In this work, unweighted ( $\omega_i = 1$ ) fits were used to determine the least squares fit dates. The constant numerical values required in order to calculate these dates and the dates determined from paired isotopes, can be found in table 1. The values for the yields  $Y_N^{136}$ ,  $Y_N^{133}$ ,  $Y_N^{132}$  and  $Y_N^{131}$  needed modification before they could be used in the calculations. These modifications are described in the next section (F) and the modified values or the required correction factors

TABLE I

## Values Used in the Calculation of Fission Xenon Ages

$T_{1/2}$ (S) :	$^{238}\text{U}$ spontaneous fission	$(8.04 \pm 0.28) \times 10^{15}$ yr.	(Segre 1951)
$T_{1/2}$ ( $\alpha$ ) :	$^{238}\text{U}$ $\alpha$ - decay	$4.51 \times 10^9$ yr.	(Lederer 1968)
$T_{1/2}$ (Co) :	$^{60}\text{Co}$ $\beta$ -decay	$5.263 \pm 0.003$ yr.	(Gorbics 1963)
$\sigma_{235}$ :	$^{235}\text{U}$ neutron fission	563.7 barns	(Critoph 1964)
$\sigma_{\text{Co}}$ :	$^{60}\text{Co}$ neutron capture	39.2 barns	(Westcott 1962)
$\sigma_{135}$ :	$^{135}\text{Xe}$ neutron capture	$(3.6 \pm 0.4) \times 10^6$ barns	(Goldberg 1966)

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$Y_{\text{N}}^{136}$	$(6.33 \pm 0.22 \pm 0.13)$ %	%
$Y_{\text{N}}^{135}$	$(6.56 \pm 0.13)$	%
$Y_{\text{N}}^{134}$	$(8.13 \pm 0.16)$	%
$Y_{\text{N}}^{133}$	$(6.70 \pm 0.13)$	%
$Y_{\text{N}}^{132}$	$(4.43 \pm 0.09)$	%
$Y_{\text{N}}^{131}$	$(2.97 \pm 0.06)$	%
$Y_{\text{N}}^{129}$	$(0.64 \pm 0.04)$	%

(Wahl 1969  
or Farrar 1962)

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$Y_{\text{S}}^{136}$	$(6.30 \pm 0.38)$	%
$Y_{\text{S}}^{134}$	$(5.14 \pm 0.31)$	%
$Y_{\text{S}}^{132}$	$(3.63 \pm 0.22)$	%
$Y_{\text{S}}^{131}$	$(0.524 \pm 0.031)$	%

(Young 1960)

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$$^{235}\text{U} / ^{238}\text{U} \quad 7.248 \times 10^{-3}$$

$$^{59}\text{Co} \text{ mass} \quad 58.93 \text{ amu}$$

$$\text{Avogadro's number} \quad 6.02252(9) \times 10^{23} \text{ atoms/gm.mole}$$


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(Lederer 1968)

are given in chapter 4.

### 3. Complications Affecting the Determination of Fission Xenon Dates.

Up to now the assumption has been made that an isotopic composition consists of three components. In the majority of cases this assumption was found to be not valid.

An obvious complication is the production, during the irradiation of a sample, of  $^{131}\text{Xe}$  which is the end product of neutron capture reactions on the nuclei  $^{130}\text{Te}$  and  $^{130}\text{Ba}$ . For samples with uranium concentrations of less than 100 p.p.m. the effect on the isotopic abundance of  $^{131}\text{Xe}$  is usually significant.

A more subtle and important complication is the preferential diffusion of the precursors of fission product xenon. This is known to enhance the isotopic abundances of xenon isotopes with long lived precursors when xenon is released at low temperatures (Kennett and Thode, 1960) and is caused by the fact that tellurium and iodine diffuse more rapidly than xenon. The two xenon isotopes most seriously affected are  $^{131}\text{Xe}$  (the half life of  $^{131\text{m}}\text{Te} = 30.0$  hours and that of  $^{131}\text{I} = 8.05$  days) and to a lesser extent  $^{132}\text{Xe}$  (the half life of  $^{132}\text{Te} = 77.7$  hours). When preferential precursor diffusion is particularly pronounced other isotopes

can also be affected.

As a result of these effects, many of the dates calculated from paired isotopes were not valid and up to five parameters rather than just three were needed in some of the least squares fits.

Convincing evidence for the complications discussed thus far was found in the present work. But, there are further possible complications which can effect fission xenon dating experiments.

When xenon is extracted from a sample by stepwise heating before the precursors,  $^{131}\text{I}$  and  $^{132}\text{Te}$ , have completely decayed, some of the  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  collected from each temperature step except the first is associated with the neutron fission xenon of the previous temperature fractions. If a large amount of neutron fission xenon is extracted from the sample in the lowest temperature steps, or if the time lapse between successive steps is long, the amounts of excess  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  from this source become significant, and the excess must be subtracted from the measured isotopic composition (see chapter 4, p. 41).

In very high uranium content minerals such as uranium ores, neutrons which are a by-product of spontaneous fission can be captured by  $^{235}\text{U}$  and  $^{238}\text{U}$  (Young and Thode, 1960).

A correction (Shukoljukov et al., 1974) must be made for the resulting neutron fission product xenon. Since in this case the decay of the long lived isotope  $^{129}\text{I}$  ( $T_{1/2} = 1.7 \times 10^7$  years) can not be neglected, neutron capture by  $^{128}\text{Te}$  can also cause enhancement of the  $^{129}\text{Xe}$  isotope abundance.

The isotopic abundance of  $^{130}\text{Xe}$  in samples which contain only small amounts of atmospheric xenon can be enhanced by the double beta decay of  $^{130}\text{Te}$  (Inghram and Reynolds, 1950). In theory (Primakov and Rosen, 1959),  $^{130}\text{Ba}$  could also contribute to the abundance of  $^{130}\text{Xe}$  through the same process. Double beta decay as it affects the other even mass xenon isotopes can be neglected since the theoretical half lives are too long.

The enhancement of the abundances of xenon isotopes affected by precursor diffusion should be reflected by a corresponding depletion of these isotopes when xenon is extracted at high temperatures. So far this effect has proved negligible.

Other complications such as contribution from the fissioning of extinct  $^{244}\text{Pu}$  or a primordial xenon component would only occur in samples of a highly unusual nature.

## F. Neutron Fission Yield Corrections

### 1. Decay Corrections to the Yields $y_N^{133}$ , $y_N^{132}$ , and $y_N^{131}$

Among the fission xenon isotopes whose abundances were measured  $^{133}\text{Xe}$  is unique since it is a radioactive ( $T_{1/2} = 5.27$  days) nuclide and thus can only result from neutron induced fission. But this also necessitated the calculation of a different fission yield for each measured isotopic composition. Furthermore, in order to observe  $^{133}\text{Xe}$  the measurements must be made before the precursors of  $^{132}\text{Xe}$  and  $^{131}\text{Xe}$  have completely decayed. Thus the neutron fission yields of these isotopes also must be corrected for the incomplete decay of the precursors.

The decay schemes and the equations which were needed to make the necessary adjustments can be found in Appendix II. The quantities which were calculated and which are given as correction factors in the results were the fractions of the absolute neutron fission chain yields (the neutron yields shown in table 1) which were present as xenon at the moment during extraction when a xenon sample was transferred from section #1 to section #2 of the sample line. The calculations were made in two steps. First the abundances of all nuclei which were present at the end of an irradiation and which



would contribute to the neutron fission yields of the xenon isotopes under discussion were calculated. Then the values of these abundances were used in the second step to calculate the neutron fission yields at the time of transfer. A small additional correction required to account for the decay of  $^{133}\text{Xe}$  between the time of transfer and the time a sample was let into the mass spectrometer was made by reducing the absolute mass 133 chain yield from 6.70% to 6.678%.

2. The  $^{135}\text{Xe}(n,\gamma)^{136}\text{Xe}$  Correction to the Yield  $Y_N^{136}$

Since  $^{135}\text{Xe}$  has an extremely large neutron capture cross section,  $3.6 \times 10^6$  barns, during an irradiation a significant amount of  $^{136}\text{Xe}$  is produced from  $^{135}\text{Xe}$  by the reaction  $^{135}\text{Xe}(n,\gamma)^{136}\text{Xe}$ . This effectively increases the neutron fission yield of  $^{136}\text{Xe}$ . Details needed to calculate the increase in the yield,  $Y_N^{136}$ , are given in Appendix III.

G. Whole Sample Isotopic Abundances

When appropriate, a whole sample xenon isotopic composition was calculated for a sample from which xenon was extracted by stepwise heating. The isotopic composition of each step was multiplied by the absolute amount of xenon collected from it. The whole sample isotopic abundance of

each individual isotope was then found by adding together the abundances of that isotope from all the steps and dividing by the total amount of xenon collected. The neutron fission yields used to determine the whole sample fission xenon dates were calculated by multiplying the neutron fission yields for each step by the amount of neutron fission xenon found in it, summing the results for each yield, and dividing by the total amount of neutron fission xenon.

## CHAPTER 4

### RESULTS

#### A. Unirradiated Samples.

The results of experiments to determine which samples (other than the zircon and the sphene) might be suitable for testing the fission xenon dating method are shown in table 2. The errors shown in this table represent one standard deviation of the mean. For  $^{132}\text{Xe}$  which originally was the normalization isotope the error was calculated from the scatter of the peak height (pk. ht.) about the plotted curve of peak height versus time using the formula

$$\sigma = \sum \left[ \frac{(\text{pk. ht. (measured)} - \text{pk. ht. (graph)})^2}{n - 2} \right]^{1/2} \quad (1)$$

where  $n$  = number of peak height measurements.

Using the same method to calculate  $\sigma$ , the errors of the remaining isotope ratios were calculated from the relation

$$\sigma_R^2 = \frac{4 \sigma^2 \left(1 + \frac{1}{2n}\right)}{n-1} \quad (2)$$

which can be derived from the error formula for a least squares fit to a straight line (Young, 1962, p.122) under the assumption that the ratio measurements are evenly spaced.

TABLE 2  
Isotopic Composition of Unirradiated Samples  
( $^{129}\text{Xe} \equiv 1.000$ )

Sample	Weight in gm.	$^{129}\text{Xe}$ 10-12cc.	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	$^{128}\text{Xe}$	$^{126}\text{Xe}$	$^{124}\text{Xe}$
Air (Nier 1950)			0.3355	0.3949	1.0170	0.8011	0.1543	1.0000	0.0726	0.00340	0.00363
KA-64-2 (carbonatite)	0.5034	8.1	0.5028 ±.0015	0.5213 ±.0018	1.1196 ±.0021	0.8206 ±.0020	0.1542 ±.0013	1.0000 ±.0034	-	-	-
St. Paul's Rocks 18-900	0.5161	20	0.3511 ±.0021	0.4019 ±.0022	1.0187 ±.0019	0.7960 ±.0028	0.1552 ±.0013	1.0000 ±.0033	0.0743 ±.0017		
St. Paul's Rocks SE-13	0.5003	80	0.3367 ±.0022	0.3956 ±.0017	1.0154 ±.0020	0.7902 ±.0024	0.1515 ±.0012	1.0000 ±.0047	0.0706 ±.0011	0.00380 ±.00028	0.00390 ±.00019
St. Paul's Rocks SF-31	0.5004	55	0.3445 ±.0017	0.3989 ±.0026	1.0159 ±.0015	0.7978 ±.0051	0.1545 ±.0016	1.0000 ±.0033	0.0750 ±.0015	-	0.00346 ±.00023
St. Paul's Rocks NE-4	0.500	18	0.3383 ±.0037	0.3906 ±.0045	1.0251 ±.0052	0.8130 ±.0078	0.1603 ±.0046	1.0000 ±.0090	-	-	-
Hualalai (dunite)	0.4868	125	0.3329 ±.0013	0.3949 ±.0023	1.0243 ±.0013	0.8035 ±.0027	0.1541 ±.0010	1.0000 ±.0035	0.0732 ±.0012	0.00362 ±.00023	0.00367 ±.00015
Reunion (dunite)	0.5022	110	0.3379 ±.0018	0.3930 ±.0029	1.0173 ±.0013	0.7974 ±.0039	0.1520 ±.0009	1.0000 ±.0071	0.0719 ±.0007	0.00314 ±.00028	0.00343 ±.00025
Anjouan (dunite) EN 237	0.5499	115	0.3370 ±.0023	0.3996 ±.0019	1.0140 ±.0020	0.8054 ±.0043	0.1535 ±.0013	1.0000 ±.0062	0.0725 ±.0010	0.00335 ±.00019	0.00361 ±.00009
Azores (dunite) AZ 175	0.5239	143	0.3471 ±.0022	0.4050 ±.0026	1.0312 ±.0027	0.8091 ±.0051	0.1543 ±.0012	1.0000 ±.0091	0.0723 ±.0008	0.00334 ±.00013	0.00359 ±.00006
Dish Hill DH 58	0.5048	48	0.3395 ±.0019	0.3999 ±.0024	1.0175 ±.0020	0.7985 ±.0037	0.1535 ±.0014	1.0000 ±.0060	0.0723 ±.0008	0.00329 ±.00015	0.00355 ±.00022
#22-500 (biotite)	0.2628	98	0.3440 ±.0015	0.3991 ±.0016	1.0238 ±.0010	0.8030 ±.0036	0.1546 ±.0013	1.0000 ±.0071	0.0716 ±.0008	0.00351 ±.00010	0.00363 ±.00013
Gill (nepheline)	0.4521	22	0.3494 ±.0025	0.4094 ±.0020	1.0072 ±.0011	0.7951 ±.0026	0.1540 ±.0017	1.0000 ±.0050	0.0732 ±.0011	0.00364 ±.00015	0.00402 ±.00023
#14-100 (biotite)	0.3111	184	0.3508 ±.0027	0.4090 ±.0029	1.0259 ±.0017	0.8074 ±.0033	0.1547 ±.0012	1.0000 ±.0091	0.0732 ±.0009	0.00330 ±.00012	0.00355 ±.00013

When  $n$  is large

$$\sigma_R \approx 2 \sigma \text{ mean} \quad (3)$$

where  $\sigma \text{ mean} = \sigma / \sqrt{n}$ .

The isotopic composition of the Reunion dunite sample is the average of the results of two experiments. The St. Paul's Rocks NE-4 results are from the second of two unirradiated sample experiments. The initial experiment indicated a very large fission xenon excess, but very little fission xenon was found in an attempt to date this sample using a stepwise heating experiment. The isotopic composition of sample KA 64-2, agrees within experimental errors with results previously obtained in this laboratory (W. B. Clarke, private communication).

The results are consistent with the interpretation that, for all samples, the xenon is composed of an atmospheric component plus a spontaneous fission component. On the basis of the excess  $^{136}\text{Xe}$  and  $^{134}\text{Xe}$  it was judged that half these samples contained enough excess spontaneous fission xenon to make fission xenon dating feasible. KA 64-2 which showed the largest fission xenon excess (partly due to a small atmospheric component), Gill nepheline which indicated a "typical excess fission xenon component", and St. Paul's Rocks NE-4 were chosen for irradiation and

subsequent analysis by stepwise heating experiments to determine their fission xenon ages.

B.       Zircons and Sphene Dates.

1.       Sample List

Table 3 lists the one sphene and four zircon samples which were dated by the fission xenon method and gives the localities from which these samples were obtained. For each sample, columns six and seven of this table show respectively the values of the measured integrated neutron flux and the calculated neutron fission yield of  $^{136}\text{Xe}$ . Sample dates expected on the basis of previous U-Th-Pb and/or Rb-Sr analyses, and the uranium contents are given in the last two columns.

2.       Sphene Sample L-6

Since the uranium content of sample L-6 was not high enough to attempt stepwise heating with the amount of sample available, this sample was dated by a single step heating experiment. The experimental and calculated results are given in table 4. The format in which the results are presented in this table should be examined closely since it is similar to the format used in the later, more complex, tables giving the stepwise heating results.

TABLE 3  
ZIRCON SAMPLES

Sample	Origin	Weight of sample (mg.)	Length of irradiation (hr.)	Activity 1% Co-Al ( $\mu\text{Ci-gm}^{-1}$ )	Integrated neutron flux ( $10^{16} \text{ n-cm}^{-2}$ )	$^{136}\text{N}$ (percent)	Expected dates* ( $10^9\text{yr.}$ )	Uranium concentration (ppm.)
L-6 (sphene)	Western Ahaggar (Tassendjanet)	24.60	10	64.24	14.23	6.92	2.1	80
M 4082	Western Ahaggar (In Ouzzal)	12.10	10	45.9	10.17	6.83	2.9-3.3 2.1 ~0	5000
K 710		16.08	10	56.9	12.61	6.88		
G 2	Eastern Pyrenees (Canigou)	25.62	3	12.43	2.75	6.59	0.6 0.3	500
Charnockite	Eastern Pyrenees (L'Agly)	57.77	3	16.08	3.56	6.60	0.3	1000

\* Private communication, C. J. Allègre. Also see references Ferrara and Gravelle (1966), Allègre et al. (1972), and Allègre and Caby (1972) for the Western Ahaggar data, and Vitrac and Allègre (1971), Vitrac (1972), and Vitrac and Allègre (1973) for the Eastern Pyrenees data.

The quantities shown in brackets below the measured isotopic composition are the neutron fission yield corrections (see chapter 3 p. 28). As an example of their use, the neutron fission yield of  $^{132}\text{Xe}$  for this sample was 0.611 times 4.43% (the mass 132 chain yield from table 1) which equals 2.71%.

The fitted isotopic composition is given so that the results of the least squares analysis (chapter 3, p. 21; appendix IV) can be compared at each isotope with the measured isotopic composition. The fitted composition was reconstructed from the calculated values of the components in the following manner: for each isotope, multiply N by the neutron fission yield, multiply S by the spontaneous fission yield, multiply "Air" by the atmospheric isotope ratio (the values in table 2 renormalized so that  $^{132}\text{Xe} = 1.000$ ), add the resulting quantities, and then add the excess if any, to get the reconstructed ratio. For this sample the differences between the fitted and measured compositions are typical of differences expected on the basis of the experimental errors.

The isotopic composition minus air is the measured isotopic composition minus the atmospheric component (as determined by the  $^{129}\text{Xe}$  and  $^{130}\text{Xe}$  abundances). Ratios of these numbers were used in equation 4 (p.21) to calculate S/N



TABLE 4  
Fission Xenon Age of Sample L-6

	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{133}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$
Measured Isotopic Composition	1.000	1.070	0.3536	0.814	0.674	0.0650	0.404
Neutron Fission Yield Corrections			(0.634)	(0.611)	(0.305)		
Fitted Isotopic Composition	1.002	1.072	0.3504	0.808	0.674	0.0631	0.409
Isotopic Composition Minus Air	0.863	0.908	0.3536	0.398	0.346	0.0018	-0.005
Least Squares Fit Parameters	N=0.0827 ±0.0014	S=0.0464 ±0.0022	Air=0.4159 ±0.0071				
		Excess $^{131}\text{Xe}$ =0.247 ±0.012					
Least Squares Fit Date	(2.98±0.12)×10 <sup>9</sup> yr.						
Dates from Paired Ratios	<u>Isotope</u>	<u>133</u>	<u>136</u>	<u>134</u>	<u>132</u>		
	136	2.90					
	134	2.87	3.01				
	132	3.01	3.44	3.24			
	131	13.0	-22.2	....	-5.49		

Xenon was extracted 103.9 hr. after the irradiation. The amount of  $^{136}\text{Xe}$  evolved from the sample between 200°C and 1440°C was  $1.3 \times 10^{-11}$  cc STP.

values from which the paired isotope dates were calculated. The composition minus air also indicates the relative abundance of xenon due to fission (85% in this case for the isotopes  $^{136}\text{Xe}$  and  $^{134}\text{Xe}$ ), and hence gives some indication of the reliability of paired isotope dates as well as the least squares fit dates.

Examination of the paired isotope dates<sup>†</sup> shows reasonable agreement among the dates calculated from pairs of the isotopes  $^{136}\text{Xe}$ ,  $^{134}\text{Xe}$  and  $^{132}\text{Xe}$ . The dates obtained from isotope pairs involving  $^{131}\text{Xe}$  indicate that this sample contained excess  $^{131}\text{Xe}$ \*. Thus a four component (N, S, Air, and Excess  $^{131}\text{Xe}$ ) least squares fit was used to fit the measured isotopic composition.

† "----" indicates the date was the log of a negative number, an undefined quantity.

\* The  $^{131}\text{Xe}/^{133}\text{Xe}$  date is the best indicator since it is unreasonably high when a sample contains excess  $^{131}\text{Xe}$ . The analogous indicators are used to show the presence of excess  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$ , and  $^{136}\text{Xe}$ . Excess  $^{133}\text{Xe}$  is indicated by low dates.

The errors in the measured isotopic composition of this and the other dated samples can be read off the graph, figure 3. The errors in the values of the least squares fit parameters were calculated from these errors by the determinant method developed in appendix IV. The least squares fit date error was calculated from the expression

$$\sigma_T = \frac{K}{\lambda_\alpha} \frac{S}{N} \frac{1}{1 + K S/N} \left( \frac{\sigma_S^2}{S^2} + \frac{\sigma_N^2}{N^2} \right)^{1/2} \quad (4)^\dagger$$

where  $K = \left( \frac{^{235}\text{U}}{^{238}\text{U}} \right) \frac{\lambda_\alpha}{\lambda_S} \sigma_{235} (\phi t)$

and where the other symbols are defined in chapter 2 and appendix IV.

The fission xenon date of this sample, verified by the consistency among the results, is the least squares fit date,  $2.98 \pm 0.12$  by. (billion years). This disagrees with the accepted date, 2.1 by. for the formation of the Tassendjanet complex (Allègre and Caby, 1972).

† This is an approximation since the covariance of the parameters N and S is not taken into account. Strictly, the quantity in the brackets should be  $\frac{\sigma_S^2}{S^2} + \frac{\sigma_N^2}{N^2} - \frac{2\sigma_{NS}}{SN}$ .

Since  $\sigma_{NS}$  is negative equation 4 underestimates the errors (by about 20%).

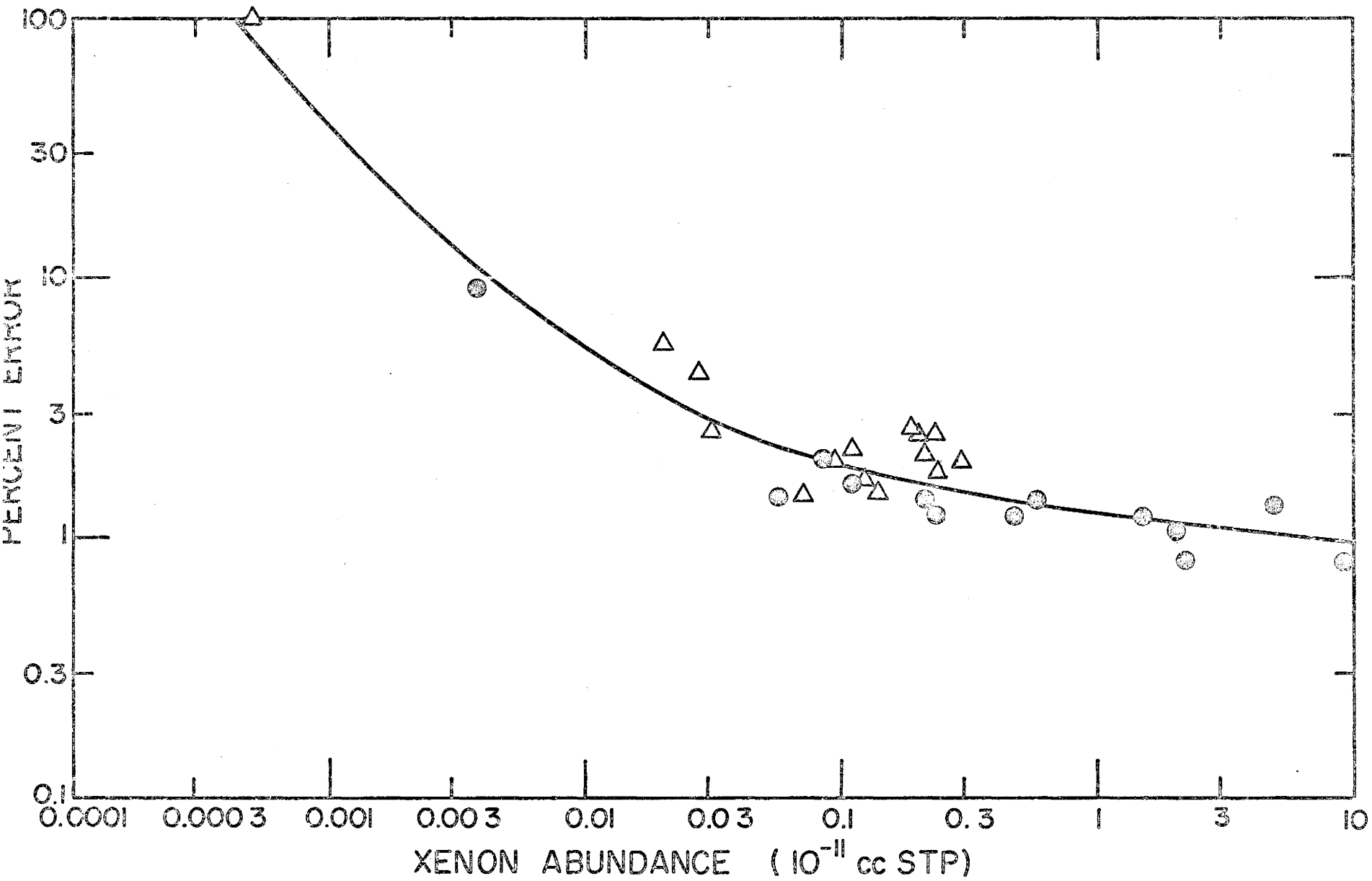


Figure 3. Relative isotopic abundance error as a function of absolute abundance.

### 3. Zircon Sample M 4082.

Xenon was extracted from sample M 4082 in a stepwise heating experiment. The results of this experiment and of the subsequent calculations are given in table 5. The errors in the isotopic abundances of the 500°C - 650°C temperature step are about three times the errors given by figure 3. The 350°C - 500°C temperature fraction was lost.

The measured isotopic compositions include small corrections ( $\lesssim 1\%$ ) for excess  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  associated with neutron fission xenon of previous temperature fractions. The method of correction using the isotope  $^{132}\text{Xe}$  as an example is as follows:

(a) for each temperature step previous to the one to be corrected multiply N (the neutron fission component) x mass 132 chain yield x absolute amount of  $^{136}\text{Xe}$  observed and sum the resulting quantities.

(b) subtract the  $^{132}\text{Xe}$  neutron fission yield correction of the previous step from that of the step to be corrected and multiply by the sum calculated in (a).

(c) multiply the isotopic abundance of  $^{132}\text{Xe}$  of the step to be corrected by the absolute amount of  $^{136}\text{Xe}$  of that step and subtract from this number the result calculated in (b).

(d) divide the result calculated in (c) by the

Date ( $\times 10^9$ yr.)	$^{136}\text{Xe}$ ( $\times 10^{-11}$ cc)	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{133}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	DATES FROM PAIRED ISOTOPES					
200°C - 350°C Temperature Step: Extracted 36 18 hr. after irradiation														
		Measured Isotopic Composition	1.070	1.183	0.516	1.070	0.753	0.1192	0.770	ISOTOPE	133	136	134	132
-0.26±0.15	1.50	Neutron Fission Yield Correction			(0.676)	(0.545)	(0.2608)			136	- .264			
		Fitted Isotopic Composition	0.978	1.199	0.508	1.061	0.723	0.1231	0.798	134	- .380	- .019		
		Isotopic Comp. Minus Air	0.772	0.884	0.516	0.287	0.136	0.0004	0.000	132	.127	.857	.529	
										131	2.99	-5.34	-----	-1.68
Least Squares Fit Parameters N=0.1125 S=0.0060 Air=0.812														
500°C - 650°C Temperature Step: Extracted 92 40 hr. after irradiation														
		Measured Isotopic Composition	1.000	1.082	0.441	1.230	0.944	0.2	0.810	ISOTOPE	133	136	134	132
0.03±0.30	1.02	Neutron Fission Yield Correction			(0.663)	(0.569)	(0.2767)			136	- .101			
		Fitted Isotopic Composition	0.973	1.153	0.390	1.193	0.826	0.144	0.932	134	-1.15	2.66		
		Isotopic Comp. Minus Air	0.728	0.762	0.441	0.406	0.295	----	0.000	132	1.44	14.3	5.98	
										131	8.46	-8.06	-----	-2.84
Least Squares Fit Parameters N=0.0962 S=0.0006 Air=0.948														
650°C - 800°C Temperature Step: Extracted 179.74 hr. after irradiation														
		Measured Isotopic Composition	1.010	1.091	0.2853	1.312	0.776	0.0985	0.677	ISOTOPE	133	136	134	132
1.78±0.10 (~0.5)	1.10	Neutron Fission Yield Correction			(0.438)	(0.802)	(0.470)			136	.791			
		Fitted Isotopic Composition	1.027	1.138	0.2359	1.201	0.753	0.1199	0.777	134	.293	2.19		
		Isotopic Comp. Minus Air	0.773	0.824	0.2853	0.624	0.234	-0.0059	0.000	132	2.98	----	----	
										131	5.74	-2.09	-8.34	.362
Least Squares Fit Parameters N=0.0806 S=0.0343 Air=0.790														
800°C - 950°C Temperature Step: Extracted 182.56 hr. after irradiation														
		Measured Isotopic Composition	1.000	1.144	0.3791	0.677	0.3067	0.0166	0.0849	ISOTOPE	133	136	134	132
0.59±0.08	1.97	Neutron Fission Yield Correction			(0.432)	(0.807)	(0.475)			136	.415			
		Fitted Isotopic Composition	1.009	1.162	0.3645	0.640	0.2884	0.0195	0.1267	134	.292	.712		
		Isotopic Comp. Minus Air	0.972	1.111	0.3791	0.590	0.2387	0.0035	0.0000	132	1.11	----	3.12	
										131	2.94	-1.40	-3.65	-1.83
Least Squares Fit Parameters N=0.1264 S=0.0163 Air=0.1288														
950°C - 1100°C Temperature Step: Extracted 186.15 hr. after irradiation														
		Measured Isotopic Composition	1.000	1.116	0.3505	0.605	0.2266	0.0024	0.0154	ISOTOPE	133	136	134	132
1.06±0.07	2.54	Neutron Fission Yield Correction			(0.424)	(0.813)	(0.482)			136	.858			
		Fitted Isotopic Composition	1.006	1.130	0.3363	0.575	0.2193	0.0066	0.0429	134	.731	1.19		
		Isotopic Comp. Minus Air	0.995	1.110	0.3505	0.589	0.2143	0.0000	0.0000	132	1.37	----	3.00	
										131	2.29	- .238	-1.62	.689
Least Squares Fit Parameters N=0.1189 S=0.0285 Air=0.4358														
1100°C - 1250°C Temperature Step: Extracted 189.53 hr. after irradiation														
		Measured Isotopic Composition	1.000	1.050	0.2504	0.551	0.1716	----	0.0062	ISOTOPE	133	136	134	132
2.58±0.08	8.81	Neutron Fission Yield Correction			(0.416)	(0.819)	(0.488)			136	2.63			
		Fitted Isotopic Composition	1.000	1.049	0.2527	0.553	0.1683	0.0010	0.0065	134	2.65	2.57		
		Isotopic Comp. Minus Air	0.998	1.047	0.2504	0.545	0.1667	----	0.0000	132	2.60	2.05	2.47	
										131	2.92	2.34	2.15	2.31
Least Squares Fit Parameters N=0.0909 S=0.0597 Air=0.0066														
1250°C - 1400°C Temperature Step: Extracted 192.28 hr. after irradiation														
		Measured Isotopic Composition	1.000	1.079	0.2388	0.550	0.1615	----	0.0032	ISOTOPE	133	136	134	132
2.82±0.08	9.60	Neutron Fission Yield Correction			(0.419)	(0.823)	(0.453)			136	2.82			
		Fitted Isotopic Composition	0.999	1.038	0.2389	0.552	0.1622	0.0002	0.0012	134	2.82	2.64		
		Isotopic Comp. Minus Air	0.999	1.037	0.2388	0.547	0.1590	----	0.0000	132	2.79	2.02	2.69	
										131	2.67	2.99	3.11	2.90
Least Squares Fit Parameters N=0.0873 S=0.0639 Air=0.0012														

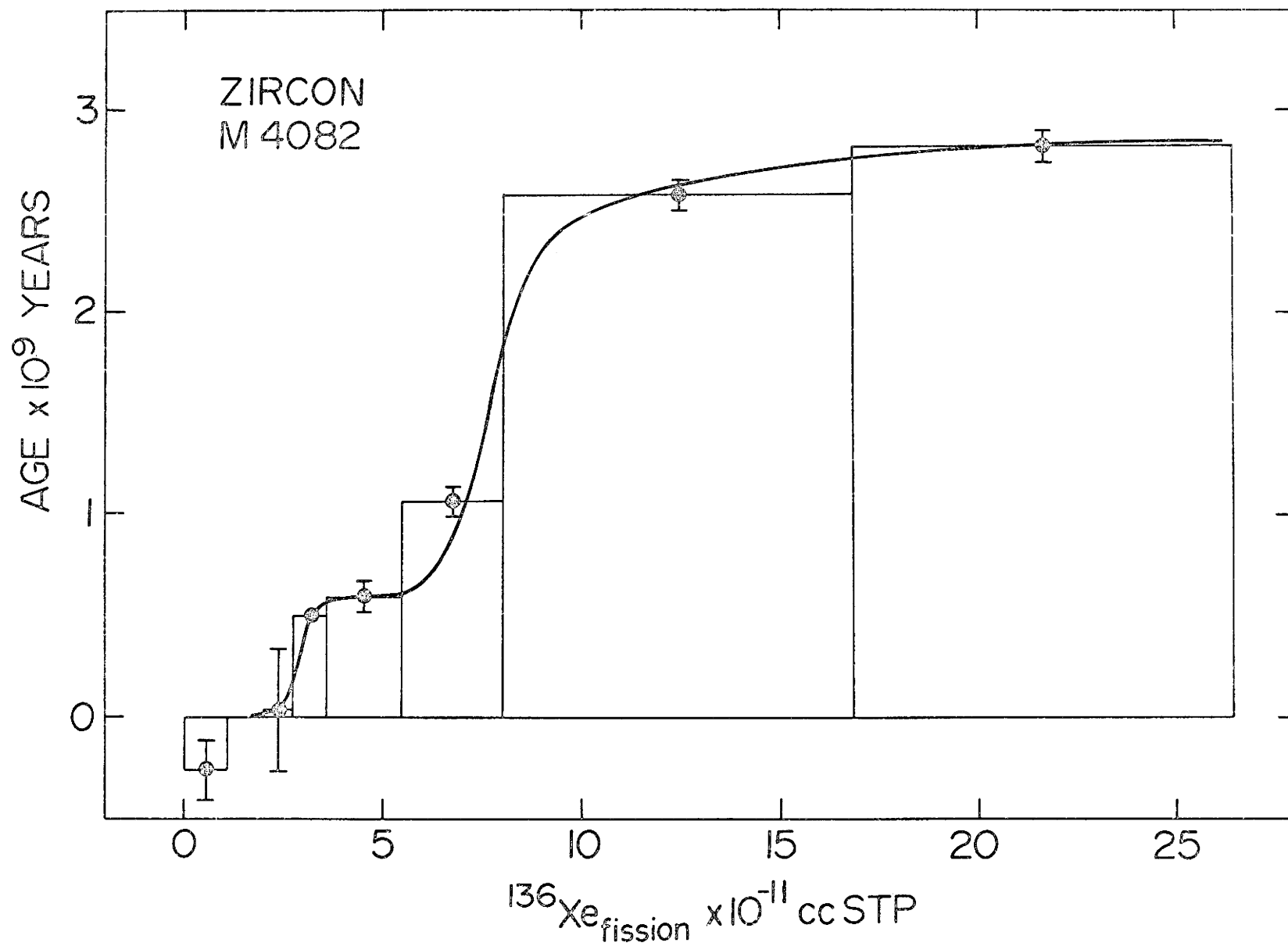
absolute amount of  $^{136}\text{Xe}$  of the step to be corrected to obtain the corrected isotopic abundance of  $^{132}\text{Xe}$ .

All the isotopic compositions of this sample were fitted to three parameter (N, S, Air) least squares fits. This was not valid for the  $650^{\circ}\text{C}$  to  $800^{\circ}\text{C}$  temperature fraction for which the best estimate of the step date is probably 0.5 by., the average of the  $^{136}\text{Xe}/^{133}\text{Xe}$  and  $^{134}\text{Xe}/^{136}\text{Xe}$  dates.

Diffusion of the precursors of  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$  and probably  $^{133}\text{Xe}$  affected the isotopic compositions of all the temperature steps except the last two. This is indicated by high  $^{131}\text{Xe}/^{133}\text{Xe}$ , high  $^{132}\text{Xe}/^{133}\text{Xe}$ , and a tendency for low  $^{134}\text{Xe}/^{136}\text{Xe}$  dates as well as by differences, which are larger than the errors, between the fitted and measured isotopic compositions. Only the date obtained from the  $650^{\circ}\text{C}$  -  $800^{\circ}\text{C}$  extraction changed significantly (from 1.78 by. to 1.06 by.) when the results were checked by five parameter (i.e. allowing for excess  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$ ) fits.

A plot of the fission xenon age versus the cumulative amount of fission  $^{136}\text{Xe}$  extracted is shown in figure 4. The smooth curve in the figure was drawn so that for each temperature step the area under the curve equals the area of the corresponding rectangle defined by the age and the amount of

Figure 4. The Fission Xenon Dates of Sample M 4082 Versus the Cumulative Amount of Fission  $^{136}\text{Xe}$  Released.





fission  $^{136}\text{Xe}$  released. The following information is apparent: (a) A prominent high temperature plateau shows an initial sample formation age of  $2.82 \pm 0.08$  by.. This is entirely consistent with the Rb-Sr whole rock age (Ferrara and Gravelle, 1966) and single zircon analysis (Lancelot et al., 1972). (b) A less prominent plateau indicates a zero age consistent with U - Th - Pb analyses (Lancelot et al., 1972). (c) A possible plateau showing an age of 0.6 by. is indicated. An event of this date has not been observed before in the area from which this sample was obtained.

#### 4. Zircon Sample K 710

The experimental and calculated results obtained from measurements of the abundances of xenon extracted from zircon sample K 710 in a stepwise heating experiment are given in table 6. The errors in the isotopic abundances of  $^{130}\text{Xe}$  of the first three temperature fractions are about twice those given in figure 3. The larger errors are a result of a very rapid variation of the  $^{130}\text{Xe}/^{136}\text{Xe}$  ratios as a function of time. Excess  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  required five parameter fits to the isotopic compositions of all the temperature steps except the last one. A four parameter fit was found to be best for the  $900^{\circ}\text{C} - 1400^{\circ}\text{C}$  fraction.

TABLE 6

FISSION XENON DATA: SAMPLE #716

DATE	$^{135}\text{Xe}$ ( $\times 10^9 \text{ yr.}^{-1}$ )	$^{136}\text{Xe}$ ( $\times 10^{-11} \text{ cc}$ )	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{133}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	DATA FROM PAIRED ISOTOPES				
200°C - 350°C TEMPERATURE STEP: EXTRACTED 104.76 HR. AFTER IRRADIATION														
19.7±0.5	0.086	MEASURED ISOTOPIC COMPOSITION	1.000	1.106	0.0054	2.784	2.191	0.3219	2.343	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.632)	(0.614)	(0.3075)			136	20.8			
		FITTED ISOTOPIC COMPOSITION	1.002	1.104	0.0065	2.784	2.191	0.3605	2.337	134	20.9	16.4		
		ISOTOPIC COMP. MINUS AIR	0.214	0.181	0.0054	0.402	0.314	-0.395	0.000	132	28.5	----	----	
									131	39.5	-22.2	----	4.28	
LEAST SQUARES FIT PARAMETERS			N=0.0015 ±0.0021	S=0.0329 ±0.0047	AIR=2.377 ±0.059	EXC.132=0.284 ±0.069	EXC.131=0.300 ±0.075							
350°C - 500°C TEMPERATURE STEP: EXTRACTED 107.81 HR. AFTER IRRADIATION														
6.98±0.41	0.132	MEASURED ISOTOPIC COMPOSITION	1.000	1.127	0.0804	2.252	1.761	0.235	1.624	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.624)	(0.625)	(0.3150)			136	8.04			
		FITTED ISOTOPIC COMPOSITION	1.026	1.095	0.0999	2.252	1.761	0.2508	1.626	134	9.10	2.46		
		ISOTOPIC COMP. MINUS AIR	0.455	0.486	0.0804	0.601	0.460	-0.155	0.000	132	13.7	----	----	
									131	24.2	-19.0	----	-4.28	
LEAST SQUARES FIT PARAMETERS			N=0.0240 ±0.0017	S=0.0502 ±0.0032	AIR=1.653 ±0.034	EXC.132=0.351 ±0.053	EXC.131=0.410 ±0.051							
500°C - 650°C TEMPERATURE STEP: EXTRACTED 111.62 HR. AFTER IRRADIATION														
0.76±0.41	0.058	MEASURED ISOTOPIC COMPOSITION	1.000	1.212	0.1760	2.432	2.104	0.434	1.945	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.614)	(0.637)	(0.3241)			136	.917			
		FITTED ISOTOPIC COMPOSITION	1.020	1.188	0.1909	2.432	2.104	0.304	1.968	134	1.99	-1.55		
		ISOTOPIC COMP. MINUS AIR	0.340	0.435	0.1760	0.431	0.527	0.130	-0.023	132	6.75	----	----	
									131	19.8	-21.7	----	-5.70	
LEAST SQUARES FIT PARAMETERS			N=0.0466 ±0.0023	S=0.0063 ±0.0044	AIR=2.002 ±0.043	EXC.132=0.277 ±0.050	EXC.131=0.479 ±0.048							
650°C - 800°C TEMPERATURE STEP: EXTRACTED 127.98 HR. AFTER IRRADIATION														
1.04±0.21	0.118	MEASURED ISOTOPIC COMPOSITION	1.000	1.148	0.3337	1.123	0.969	0.1301	0.866	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.570)	(0.686)	(0.3622)			136	1.06			
		FITTED ISOTOPIC COMPOSITION	1.003	1.145	0.3358	1.123	0.969	0.1336	0.866	134	1.14	.865		
		ISOTOPIC COMP. MINUS AIR	0.710	0.806	0.3337	0.242	0.275	-0.0035	0.000	132	-4.84	-3.67	-2.01	
									131	9.94	-9.32	----	-6.08	
LEAST SQUARES FIT PARAMETERS			N=0.0882 ±0.0024	S=0.0167 ±0.0036	AIR=0.881 ±0.015	EXC.132=-0.087 ±0.028	EXC.131=0.171 ±0.024							
800°C - 950°C TEMPERATURE STEP: EXTRACTED 130.55 HR. AFTER IRRADIATION														
2.35±0.27	0.055	MEASURED ISOTOPIC COMPOSITION	1.000	1.041	0.2771	1.326	1.179	0.1344	0.914	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.563)	(0.694)	(0.368)			136	2.06			
		FITTED ISOTOPIC COMPOSITION	0.973	1.075	0.2549	1.326	1.179	0.1402	0.909	134	1.20	5.15		
		ISOTOPIC COMP. MINUS AIR	0.695	0.693	0.2771	0.402	0.451	-0.0058	0.005	132	3.07	23.2	8.36	
									131	14.9	-13.2	----	-6.11	
LEAST SQUARES FIT PARAMETERS			N=0.0678 ±0.0025	S=0.0320 ±0.0042	AIR=0.924 ±0.023	EXC.132=0.078 ±0.030	EXC.131=0.360 ±0.027							
950°C - 1400°C TEMPERATURE STEP: EXTRACTED 134.90 HR. AFTER IRRADIATION														
1.89±0.10	1.34	MEASURED ISOTOPIC COMPOSITION	1.000	1.089	0.3757	0.623	0.3044	0.0269	0.1736	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.551)	(0.705)	(0.378)			136	1.93			
		FITTED ISOTOPIC COMPOSITION	0.996	1.090	0.3760	0.628	0.3044	0.0262	0.1695	134	1.89	2.03		
		ISOTOPIC COMP. MINUS AIR	0.943	1.022	0.3757	0.451	0.1686	0.0007	-0.0041	132	1.84	1.40	1.75	
									131	4.27	-1.17	-6.32	-3.49	
LEAST SQUARES FIT PARAMETERS			N=0.1021 ±0.0016	S=0.0376 ±0.0022	AIR=0.1724 ±0.0042	EXC.131=0.344 ±0.048								
WHOLE SAMPLE														
2.0±1.12	1.79	MEASURED ISOTOPIC COMPOSITION	1.000	1.099	0.3238	0.960	0.632	0.0797	0.511	ISOTOPE	133	136	134	132
		NEUTRON FISSION YIELD CORRECTION			(0.556)	(0.701)	(0.3742)			136	2.10			
		FITTED ISOTOPIC COMPOSITION	1.051	1.098	0.3244	0.960	0.632	0.0788	0.511	134	2.12	2.05		
		ISOTOPIC COMP. MINUS AIR	0.829	0.898	0.3238	0.441	0.222	0.0009	0.000	132	2.60	6.77	3.60	
									131	8.18	-5.62	----	2.51	
LEAST SQUARES FIT PARAMETERS			N=0.0874 ±0.0015	S=0.0361 ±0.0021	AIR=0.520 ±0.006	EXC.132=0.938 ±0.013	EXC.131=0.106 ±0.009							

The step fission xenon dates are shown in figure 5 as a function of the cumulative amount of  $^{136}\text{Xe}$  extracted. The pattern, very high dates obtained from the first two temperature fractions followed by three dates increasing from a too low to a too high date and then a prominent high temperature plateau, should be noted. Since the high temperature age,  $1.89 \pm 0.10$  by., is not too different from the whole sample age,  $2.09 \pm 0.12$  by., the pattern is typical of that to be expected in a graph of fission xenon dates obtained from an undisturbed sample.

#### 5. Charnockite Zircon Sample

The information obtained from the charnockite zircon sample is presented in table 7. The isotopic compositions of the  $200^{\circ}\text{C} - 350^{\circ}\text{C}$ ,  $500^{\circ}\text{C} - 650^{\circ}\text{C}$ , and  $950^{\circ}\text{C} - 1100^{\circ}\text{C}$  xenon fractions which contained excess  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  were analyzed by five parameter fits. A three component analysis was adequate for each of the remaining compositions.

The sample age versus the cumulative amount of  $^{136}\text{Xe}$  released is plotted in figure 6. Note that, although the pattern superficially follows that of figure 5, there are two differences: (a) the dates obtained from the lower temperature steps when compared with the plateau age are much higher, (b) the date from the fourth step rather than

Figure 5. The Fission Xenon Dates of Sample K 710 Versus the Cumulative Amount of Fission  $^{136}\text{Xe}$  Released.

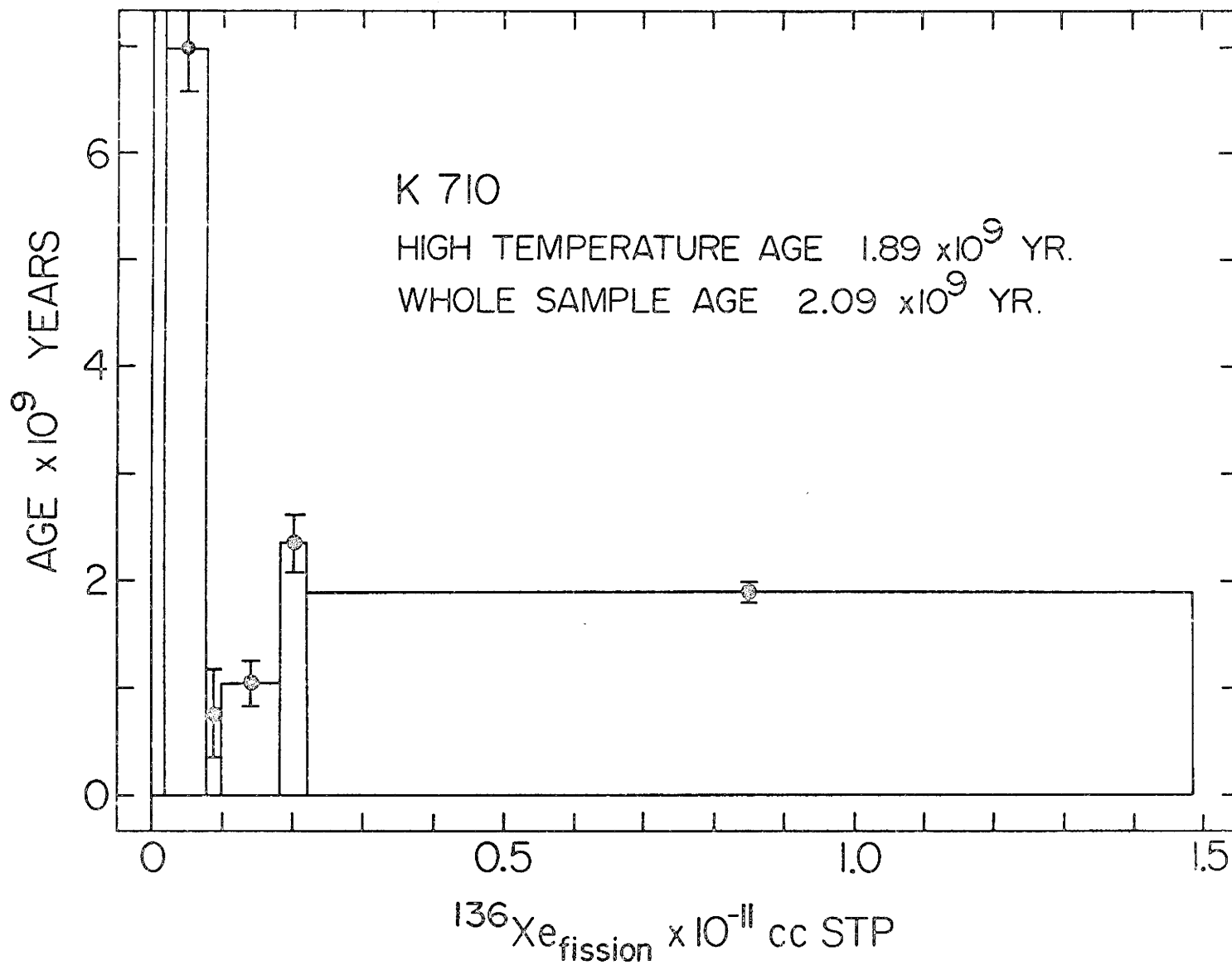
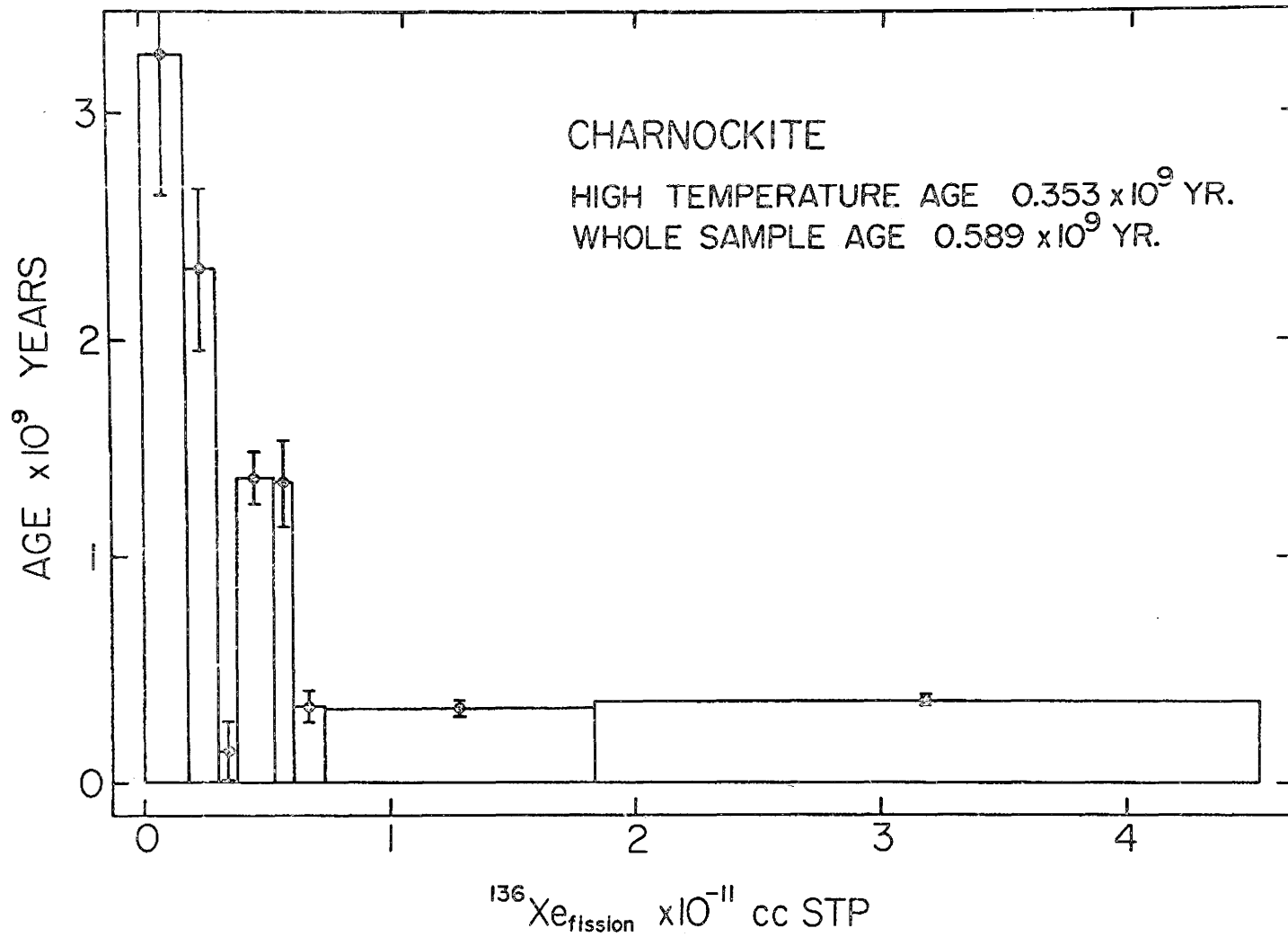


TABLE 7  
FISSION XENON DATES CHAMPACKITE SAMPLE

DATE ( $10^6$ YR.)	$^{136}\text{Xe}$ ( $\times 10^{-11}$ CC)	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{133}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	DATES FROM PAIRED ISOTOPES	
250°C - 350°C TEMPERATURE STEP; EXTRACTED 134.43 HR. AFTER IRRADIATION										
1.26±0.63	1.78	MEASURED ISOTOPIIC COMPOSITION	1.000	1.182	0.0105	2.810	2.088	0.3978	2.567	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.562)	(0.695)	(0.3689)			136   6.63
		FITTED ISOTOPIIC COMPOSITION	1.017	1.161	0.0261	2.810	2.088	0.3964	2.570	134   8.37 .099
		ISOTOPIIC COMP. MINUS AIR	0.139	0.168	0.0105	0.200	0.032	0.0218	0.000	132   11.5 -2.38 -7.64
LEAST SQUARES FIT PARAMETERS N=0.0049 S=0.0174 AIR=2.613 EXC.132=0.112 EXC.131=0.013 ±.0024 ±.0025 ±.025 ±.035 ±.028										
350°C - 500°C TEMPERATURE STEP; EXTRACTED 138.6 HR. AFTER IRRADIATION										
2.32±0.36	0.43	MEASURED ISOTOPIIC COMPOSITION	1.000	1.199	0.0121	2.317	1.824	0.3304	2.145	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.551)	(0.706)	(0.3782)			136   9.39
		FITTED ISOTOPIIC COMPOSITION	1.020	1.142	0.0638	2.357	1.767	0.3335	2.162	134   11.5 .049
		ISOTOPIIC COMP. MINUS AIR	0.281	0.342	0.0121	0.136	0.106	-0.0005	0.000	132   8.54 .185 .099
LEAST SQUARES FIT PARAMETERS N=0.0113 S=0.0287 AIR=2.199 ±.0013 ±.0037 ±.016										
500°C - 650°C TEMPERATURE STEP; EXTRACTED 142.18 HR. AFTER IRRADIATION										
0.14±0.14	0.201	MEASURED ISOTOPIIC COMPOSITION	1.000	1.156	0.1879	2.132	1.658	0.3054	1.923	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.541)	(0.715)	(0.3860)			136   .062
		FITTED ISOTOPIIC COMPOSITION	0.990	1.173	0.1740	2.127	1.658	0.2973	1.927	134   -.167 .665
		ISOTOPIIC COMP. MINUS AIR	0.355	0.397	0.1879	0.178	0.118	0.0087	0.000	132   .119 .485 .558
LEAST SQUARES FIT PARAMETERS N=0.0481 S=0.0040 AIR=1.960 EXC.131=0.057 ±.0024 ±.0040 ±.029 ±.026										
650°C - 800°C TEMPERATURE STEP; EXTRACTED 157.2 HR. AFTER IRRADIATION										
1.36±0.12	0.294	MEASURED ISOTOPIIC COMPOSITION	1.000	1.133	0.1118	1.652	1.228	0.2103	1.363	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.502)	(0.751)	(0.418)			136   2.18
		FITTED ISOTOPIIC COMPOSITION	1.004	1.107	0.1486	1.689	1.177	0.2120	1.374	134   2.59 .810
		ISOTOPIIC COMP. MINUS AIR	0.543	0.595	0.1118	0.267	0.136	0.0001	0.000	132   1.87 -.280 .390
LEAST SQUARES FIT PARAMETERS N=0.0441 S=0.0397 AIR=1.398 ±.0023 ±.0034 ±.012										
800°C - 950°C TEMPERATURE STEP; EXTRACTED 160.16 HR. AFTER IRRADIATION										
1.34±0.20	0.183	MEASURED ISOTOPIIC COMPOSITION	1.000	1.179	0.1128	2.097	1.480	0.2862	1.768	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.494)	(0.757)	(0.424)			136   1.24
		FITTED ISOTOPIIC COMPOSITION	1.037	1.161	0.1184	2.057	1.497	0.2764	1.792	134   1.64 .239
		ISOTOPIIC COMP. MINUS AIR	0.399	0.471	0.1128	0.275	0.044	0.0097	-0.024	132   1.88 -3.72 2.93
LEAST SQUARES FIT PARAMETERS N=0.0359 S=0.0315 AIR=1.822 ±.0023 ±.0044 ±.019										
950°C - 1100°C TEMPERATURE STEP; EXTRACTED 163.01 HR. AFTER IRRADIATION										
0.341±0.074	0.215	MEASURED ISOTOPIIC COMPOSITION	1.000	1.174	0.2549	1.479	1.075	0.1942	1.093	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.487)	(0.763)	(0.430)			136   .344
		FITTED ISOTOPIIC COMPOSITION	1.003	1.172	0.2565	1.477	1.075	0.1746	1.132	134   .368 .287
		ISOTOPIIC COMP. MINUS AIR	0.620	0.727	0.2549	0.328	0.168	0.0196	-0.039	132   .363 .575 .354
LEAST SQUARES FIT PARAMETERS N=0.0769 S=0.0163 AIR=1.151 EXC.131=0.059 EXC.129=-.035 ±.0026 ±.0036 ±.013 ±.018										
1100°C - 1250°C TEMPERATURE STEP; EXTRACTED 165.72 HR. AFTER IRRADIATION										
0.330±0.036	1.12	MEASURED ISOTOPIIC COMPOSITION	1.000	1.138	0.3994	0.599	0.2485	0.01536	0.0990	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.480)	(0.769)	(0.435)			136   .306
		FITTED ISOTOPIIC COMPOSITION	0.989	1.150	0.3893	0.601	0.2476	0.01500	0.0972	134   .226 .506
		ISOTOPIIC COMP. MINUS AIR	0.967	1.099	0.3994	0.501	0.1706	0.00036	0.0018	132   .279 .038 .375
LEAST SQUARES FIT PARAMETERS N=0.1214 S=0.0243 AIR=0.0989 ±.0021 ±.0027 ±.0036										
1250°C - 1400°C TEMPERATURE STEP; EXTRACTED 168.54 HR. AFTER IRRADIATION										
0.362±0.029	2.72	MEASURED ISOTOPIIC COMPOSITION	1.000	1.150	0.3942	0.540	0.1949	---	0.0151	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.473)	(0.775)	(0.441)			136   .359
		FITTED ISOTOPIIC COMPOSITION	0.996	1.155	0.3918	0.542	0.1900	0.0026	0.0166	134   .335 .418
		ISOTOPIIC COMP. MINUS AIR	0.995	1.144	0.3942	0.524	0.183	---	0.0000	132   .349 .239 .375
LEAST SQUARES FIT PARAMETERS N=0.1240 S=0.0273 AIR=0.0169 ±.0017 ±.0022 ±.0026										
WHOLE SAMPLE										
0.589±0.046	6.44	MEASURED ISOTOPIIC COMPOSITION	1.000	1.159	0.2615	1.296	0.648	0.1386	0.883	ISOTOPE   133   136   134   132
		NEUTRON FISSION YIELD CORRECTION			(0.502)	(0.749)	(0.418)			136   .600
		FITTED ISOTOPIIC COMPOSITION	1.011	1.153	0.2670	1.284	0.836	0.1389	0.901	134   .671 .422
		ISOTOPIIC COMP. MINUS AIR	0.698	0.802	0.2615	0.369	0.126	-0.0003	0.018	132   .682 1.93 .703
LEAST SQUARES FIT PARAMETERS N=0.0797 S=0.0291 AIR=0.916 ±.0017 ±.0023 ±.007										

Figure 6. The fission xenon dates of the Charnockite sample versus the cumulative amount of fission  $^{136}\text{Xe}$  released.



being lower is the same as that from the fifth step. The difference between the whole sample age, 0.589 by., and the high temperature age,  $0.353 \pm 0.024$  by. indicates that this is a disturbed sample. The results are in agreement with the Rb-Sr (Vitrac and Allègre, 1971) and U-Pb (Vitrac, 1972) dates of the charnockite.

#### 6. Zircon Sample G 2

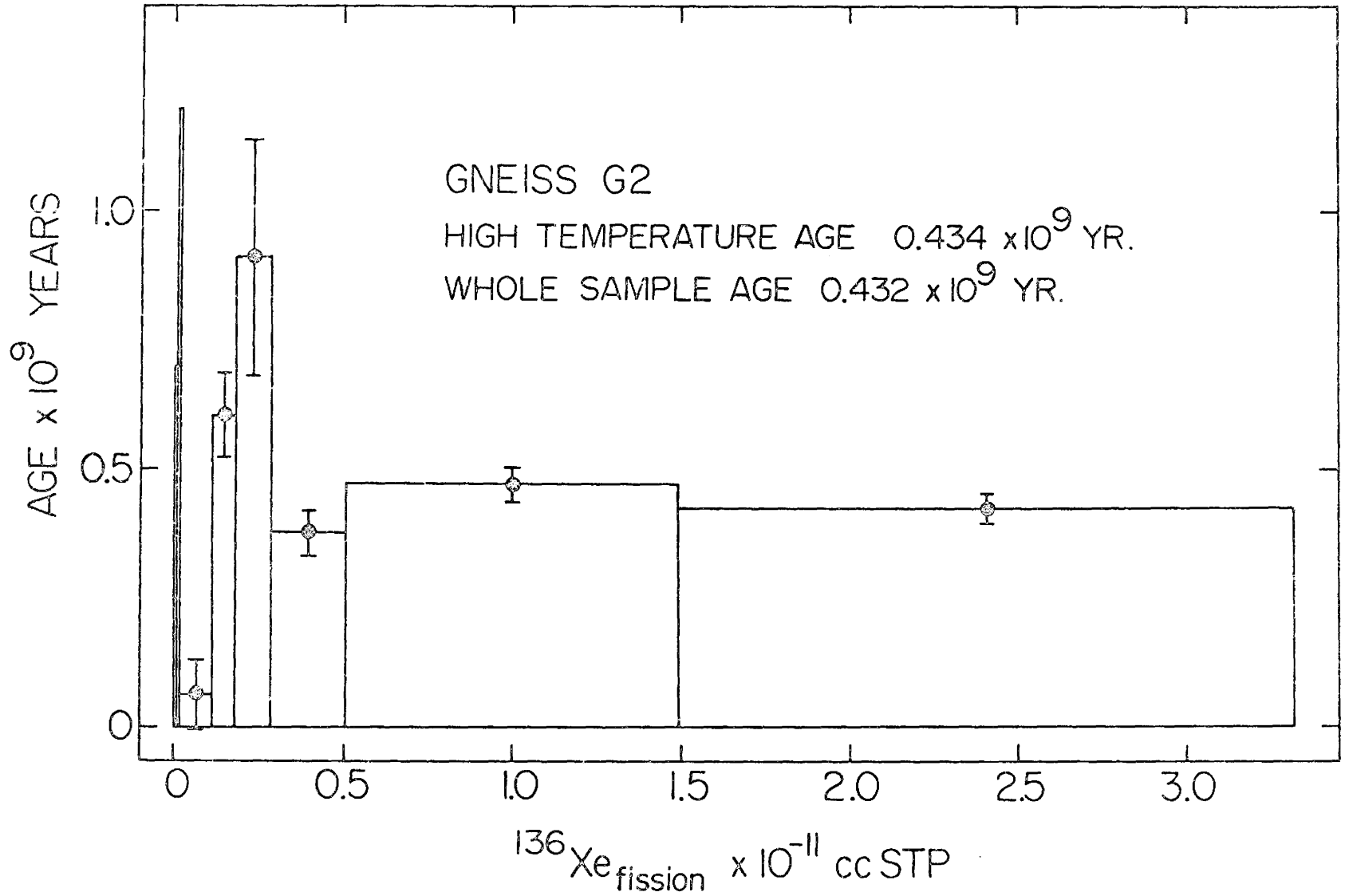
Data obtained from sample G 2 are given in table 8. The two lowest temperature steps,  $200^{\circ}\text{C} - 350^{\circ}\text{C}$  and  $350^{\circ}\text{C} - 500^{\circ}\text{C}$ , did not contain enough fission xenon to give meaningful paired isotope dates. A five parameter fit was found to be best for the  $350^{\circ}\text{C} - 500^{\circ}\text{C}$  step. Four parameter fits were used for the  $200^{\circ}\text{C} - 350^{\circ}\text{C}$  and  $650^{\circ}\text{C} - 800^{\circ}\text{C}$  fractions. The  $800^{\circ}\text{C} - 950^{\circ}\text{C}$  isotopic composition could only be fitted if allowance was made for a depletion of the  $^{133}\text{Xe}$  abundance. The depletion of  $^{133}\text{Xe}$  is manifested by the too high  $^{136}\text{Xe}/^{133}\text{Xe}$  dates. The other isotopic compositions were fitted with three component least squares fits.

A plot of the sample age versus the cumulative amount of  $^{136}\text{Xe}$  released is shown in figure 7. Except for the smaller amount of fission xenon released at low temperatures the pattern is very similar to that shown in figure 5. Although the agreement between the high

DATE ( $\times 10^3$ yr.)	$^{136}\text{Xe}$ ( $\times 10^{-11}$ CC)	$^{133}\text{Xe}$	$^{134}\text{Xe}$	$^{135}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	DATES FROM PAIRED ISOTOPES	
300°C - 350°C TEMPERATURE STEP: EXTRACTED 148.15 HR. AFTER IRRADIATION										
0.7±1.2	0.214	MEASURED ISOTOPIC COMPOSITION	1.600	1.187	0.0177	2.957	2.434	0.443	2.855	
		NEUTRON FISSION YIELD CORRECTION			(0.525)	(0.730)	(0.3989)			
		FITTED ISOTOPIC COMPOSITION	1.010	1.185	0.0167	2.942	2.434	0.442	2.868	
		ISOTOPIC COMP. MINUS AIR	0.138	0.055	0.0177	0.041	0.137	0.001	-0.03	
		LEAST SQUARES FIT PARAMETERS N=0.0048 ±0.0027	S=0.0027 ±0.0028	AIR=2.916 ±0.025	EXC.131=0.129 ±0.038					
350°C - 500°C TEMPERATURE STEP: EXTRACTED 151.85 HR. AFTER IRRADIATION										
1.20±0.86	0.118	MEASURED ISOTOPIC COMPOSITION	1.000	1.176	0.0170	2.910	2.370	0.460	2.749	
		NEUTRON FISSION YIELD CORRECTION			(0.516)	(0.739)	(0.407)			
		FITTED ISOTOPIC COMPOSITION	1.004	1.171	0.0214	2.910	2.370	0.425	2.755	
		ISOTOPIC COMP. MINUS AIR	0.076	0.088	0.0170	0.108	0.163	0.035	-0.006	
		LEAST SQUARES FIT PARAMETERS N=0.0062 ±0.0025	S=0.0061 ±0.0042	AIR=2.802 ±0.051	EXC.132=0.065 ±0.067	EXC.131=0.152 ±0.051				
500°C - 650°C TEMPERATURE STEP: EXTRACTED 154.87 HR. AFTER IRRADIATION										
0.054±0.067	0.186	MEASURED ISOTOPIC COMPOSITION	1.000	1.194	0.244	1.748	1.289	0.243	1.463	
		NEUTRON FISSION YIELD CORRECTION			(0.508)	(0.746)	(0.413)			
		FITTED ISOTOPIC COMPOSITION	0.993	1.194	0.248	1.753	1.272	0.227	1.474	
		ISOTOPIC COMP. MINUS AIR	0.506	0.612	0.244	0.249	0.108	0.015	-0.011	
		LEAST SQUARES FIT PARAMETERS N=0.0730 ±0.0026	S=0.0036 ±0.0032	AIR=1.499 ±0.013						
650°C - 800°C TEMPERATURE STEP: EXTRACTED 157.09 HR. AFTER IRRADIATION										
0.604±0.082	0.117	MEASURED ISOTOPIC COMPOSITION	1.000	1.140	0.2000	1.494	1.091	0.1745	1.185	
		NEUTRON FISSION YIELD CORRECTION			(0.502)	(0.751)	(0.418)			
		FITTED ISOTOPIC COMPOSITION	0.998	1.130	0.2106	1.511	1.091	0.1807	1.171	
		ISOTOPIC COMP. MINUS AIR	0.607	0.677	0.2000	0.302	0.153	-0.062	0.014	
		LEAST SQUARES FIT PARAMETERS N=0.0628 ±0.0028	S=0.0034 ±0.0041	AIR=1.301 ±0.016	EXC.131=0.059 ±0.024					
800°C - 950°C TEMPERATURE STEP: EXTRACTED 159.90 HR. AFTER IRRADIATION										
0.912±0.23	0.183	MEASURED ISOTOPIC COMPOSITION	1.000	1.135	0.0994	1.644	1.224	0.2110	1.254	
		NEUTRON FISSION YIELD CORRECTION			(0.495)	(0.757)	(0.424)			
		FITTED ISOTOPIC COMPOSITION	1.019	1.130	0.0994	1.617	1.224	0.1972	1.278	
		ISOTOPIC COMP. MINUS AIR	0.571	0.630	0.0994	0.344	0.200	0.0138	-0.024	
		LEAST SQUARES FIT PARAMETERS N=0.0522 ±0.0073	S=0.0391 ±0.0094	AIR=1.300 ±0.019	EXC.133=-0.073 ±0.024	EXC.131=0.114 ±0.023				
950°C - 1100°C TEMPERATURE STEP: EXTRACTED 162.92 HR. AFTER IRRADIATION										
0.377±0.043	0.284	MEASURED ISOTOPIC COMPOSITION	1.000	1.137	0.2920	1.063	0.670	0.1091	0.672	
		NEUTRON FISSION YIELD CORRECTION			(0.487)	(0.763)	(0.430)			
		FITTED ISOTOPIC COMPOSITION	0.990	1.138	0.2951	1.080	0.662	0.1025	0.665	
		ISOTOPIC COMP. MINUS AIR	0.777	0.875	0.2920	0.387	0.137	0.0066	0.007	
		LEAST SQUARES FIT PARAMETERS N=0.0907 ±0.0021	S=0.0269 ±0.0031	AIR=0.676 ±0.008						
1100°C - 1250°C TEMPERATURE STEP: EXTRACTED 165.90 HR. AFTER IRRADIATION										
0.470±0.033	1.01	MEASURED ISOTOPIC COMPOSITION	1.000	1.101	0.3482	0.569	0.2201	0.0142	0.0825	
		NEUTRON FISSION YIELD CORRECTION			(0.480)	(0.769)	(0.436)			
		FITTED ISOTOPIC COMPOSITION	0.985	1.108	0.3445	0.585	0.2172	0.0110	0.0712	
		ISOTOPIC COMP. MINUS AIR	0.976	1.073	0.3482	0.496	0.1630	0.0033	0.0113	
		LEAST SQUARES FIT PARAMETERS N=0.1075 ±0.0021	S=0.0401 ±0.0028	AIR=0.0724 ±0.0039						
1250°C - 1400°C TEMPERATURE STEP: EXTRACTED 168.82 HR. AFTER IRRADIATION										
0.422±0.028	1.85	MEASURED ISOTOPIC COMPOSITION	1.000	1.120	0.3568	0.550	0.2010	---	0.0381	
		NEUTRON FISSION YIELD CORRECTION			(0.473)	(0.775)	(0.442)			
		FITTED ISOTOPIC COMPOSITION	0.992	1.124	0.3560	0.559	0.1952	0.0053	0.0344	
		ISOTOPIC COMP. MINUS AIR	0.988	1.107	0.3568	0.515	0.1734	---	0.0037	
		LEAST SQUARES FIT PARAMETERS N=0.1128 ±0.0019	S=0.0377 ±0.0025	AIR=0.0350 ±0.0035						
WHOLE SAMPLE										
0.432±0.031	1.96	MEASURED ISOTOPIC COMPOSITION	1.000	1.126	0.2997	0.926	0.549	0.0776	0.485	
		NEUTRON FISSION YIELD CORRECTION			(0.478)	(0.771)	(0.437)			
		FITTED ISOTOPIC COMPOSITION	0.992	1.130	0.3026	0.938	0.531	0.0754	0.489	
		ISOTOPIC COMP. MINUS AIR	0.836	0.933	0.2997	0.429	0.158	0.0024	-0.004	
		LEAST SQUARES FIT PARAMETERS N=0.0947 ±0.0017	S=0.0334 ±0.0023	AIR=0.487 ±0.005						



Figure 7. The Fission Xenon Dates of Sample G 2 Versus the Cumulative Amount of Fission  $^{136}\text{Xe}$  Released.



temperature plateau age,  $0.434 \pm 0.020$  by., and the whole sample data,  $0.432 \pm 0.031$  by., does not indicate disturbance, U-Th-Pb dating resulted in discordant ages (Allègre, private communication).

### C. Normal Rock Sample Dates

Attempts were made to date three rocks of normal composition (i.e. no unusually large uranium concentration). Of these three sufficient precision was achieved only for the carbonatite sample, KA 64 - 2, which contained a relatively small atmospheric component. The weight of this sample was 1.276 gm., the integrated neutron flux was  $2.07 \times 10^{16} \text{ n - cm}^{-2}$ , and the yield  $Y_N^{136}$  used to calculate the dates was 6.55%. The results obtained from this sample are shown in table 9. No significant amount of fission xenon was observed in the  $20^\circ\text{C} - 200^\circ\text{C}$  fraction. The isotopic compositions of the  $650^\circ\text{C} - 800^\circ\text{C}$  and  $1250^\circ\text{C} - 1400^\circ\text{C}$  xenon was not consistent with the theory on which the least squares analysis was based and could not be fitted. Figure 8 shows that the neutron fission xenon and spontaneous fission xenon released at these temperatures were not correlated, while the low  $^{134}\text{Xe}/^{136}\text{Xe}$  and  $^{132}\text{Xe}/^{136}\text{Xe}$  ratios indicate that the spontaneous fission xenon component was fractionated.

TABLE 9

FISSION XENON DATES: SAMPLE KA64-2

DATE ( $\times 10^3$ yr.)	$^{136}\text{Xe}$ ( $\times 10^{-11}$ CC)	$^{136}\text{Xe}$	$^{134}\text{Xe}$	$^{133}\text{Xe}$	$^{132}\text{Xe}$	$^{131}\text{Xe}$	$^{130}\text{Xe}$	$^{129}\text{Xe}$	DATES FROM PAIRED ISOTOPPS				
20°C - 200°C TEMPERATURE STEP: EXTRACTED 99.87 HR. AFTER IRRADIATION													
0.88		1.000	1.181	0.0030	3.057	2.443	0.465	3.010					
MEASURED ISOTOPIIC COMPOSITION													
NO SIGNIFICANT FISSION COMPONENT													
200°C - 350°C TEMPERATURE STEP: EXTRACTED 92.64 HR. AFTER IRRADIATION													
1.20±0.98	0.138	1.000	1.163	0.0237	2.852	2.974	0.456	2.760	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0048 S=0.0065 AIR=2.814 EXC.131=0.750 ±.0025 ±.0047 ±.028 ±.044													
350°C - 500°C TEMPERATURE STEP: EXTRACTED 96.63 HR. AFTER IRRADIATION													
2.12±0.32	0.095	1.000	1.125	0.0606	2.288	2.973	0.2957	1.903	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0155 S=0.0422 AIR=1.938 EXC.132=0.155 EXC.131=1.410 ±.0017 ±.0032 ±.026 ±.039 ±.046													
500°C - 650°C TEMPERATURE STEP: EXTRACTED 99.54 HR. AFTER IRRADIATION													
1.65±0.09	0.259	1.000	1.038	0.1432	1.559	2.162	0.1684	1.091	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0336 S=0.0646 AIR=1.110 EXC.132=0.126 EXC.131=1.224 ±.0036 ±.0028 ±.020 ±.033 ±.040													
650°C - 800°C TEMPERATURE STEP: EXTRACTED 114.2 HR. AFTER IRRADIATION													
0.401		1.000	0.687	0.0295	0.689	1.145	0.0583	0.3147					
MEASURED ISOTOPIIC COMPOSITION													
FRACTIONATED SPONTANEOUS FISSION XENON COMPONENT													
800°C - 950°C TEMPERATURE STEP: EXTRACTED 144.53 HR. AFTER IRRADIATION													
1.82±0.19	0.095	1.000	1.026	0.1006	1.827	2.447	0.2367	1.455	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0245 S=0.0525 AIR=1.479 EXC.132=0.079 EXC.131=1.226 ±.0023 ±.0037 ±.022 ±.033 ±.038													
950°C - 1100°C TEMPERATURE STEP: EXTRACTED 147.37 HR. AFTER IRRADIATION													
1.23±0.16	0.062	1.000	1.078	0.1166	1.842	4.449	0.2792	1.554	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0309 S=0.0426 AIR=1.587 EXC.131=3.140 ±.0030 ±.0047 ±.022 ±.069													
1100°C - 1250°C TEMPERATURE STEP: EXTRACTED 162.08 HR. AFTER IRRADIATION													
1.56±0.09	0.252	1.000	0.987	0.1525	1.219	1.335	0.1373	0.800	ISOTOPE	133	136	134	132
MEASURED ISOTOPIIC COMPOSITION													
NEUTRON FISSION YIELD CORRECTION													
FITTED ISOTOPIIC COMPOSITION													
ISOTOPIIC COMP. MINUS AIR													
LEAST SQUARES FIT PARAMETERS N=0.0398 S=0.0719 AIR=0.818 EXC.131=0.602 ±.0020 ±.0031 ±.011 ±.019													
1250°C - 1400°C TEMPERATURE STEP: EXTRACTED 165.04 HR. AFTER IRRADIATION													
		1.000	0.732	0.0420	0.753	0.662	0.520	0.2774					
MEASURED ISOTOPIIC COMPOSITION													
FRACTIONATED SPONTANEOUS FISSION XENON COMPONENT													

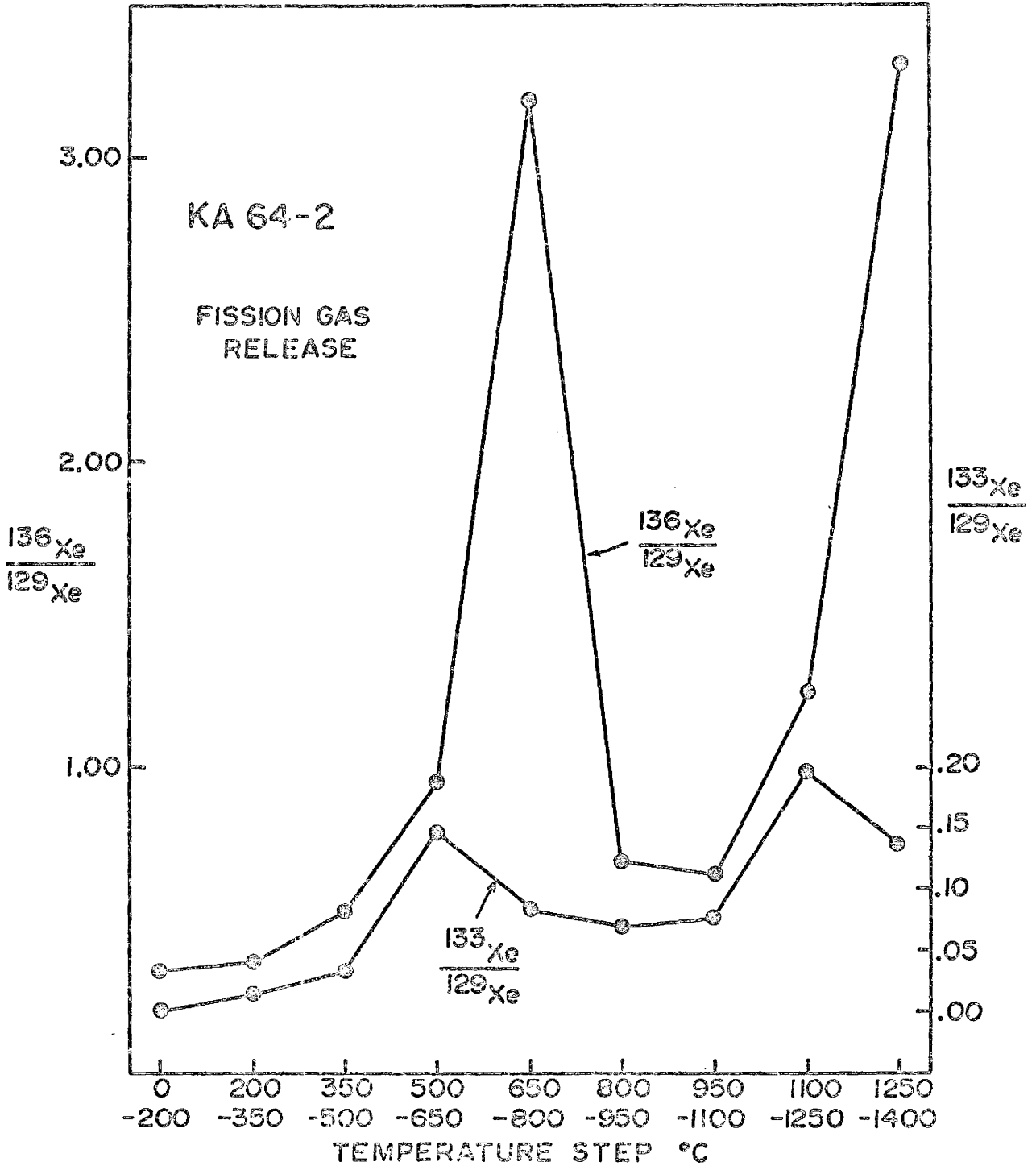


Figure 8. The correlation of neutron fission product xenon and spontaneous fission product xenon from sample KA 64-2.

Figure 9. The Fission Xenon Dates of Sample KA 64-2 Versus the Cumulative Amount of Fission  $^{136}\text{Xe}$  Released.

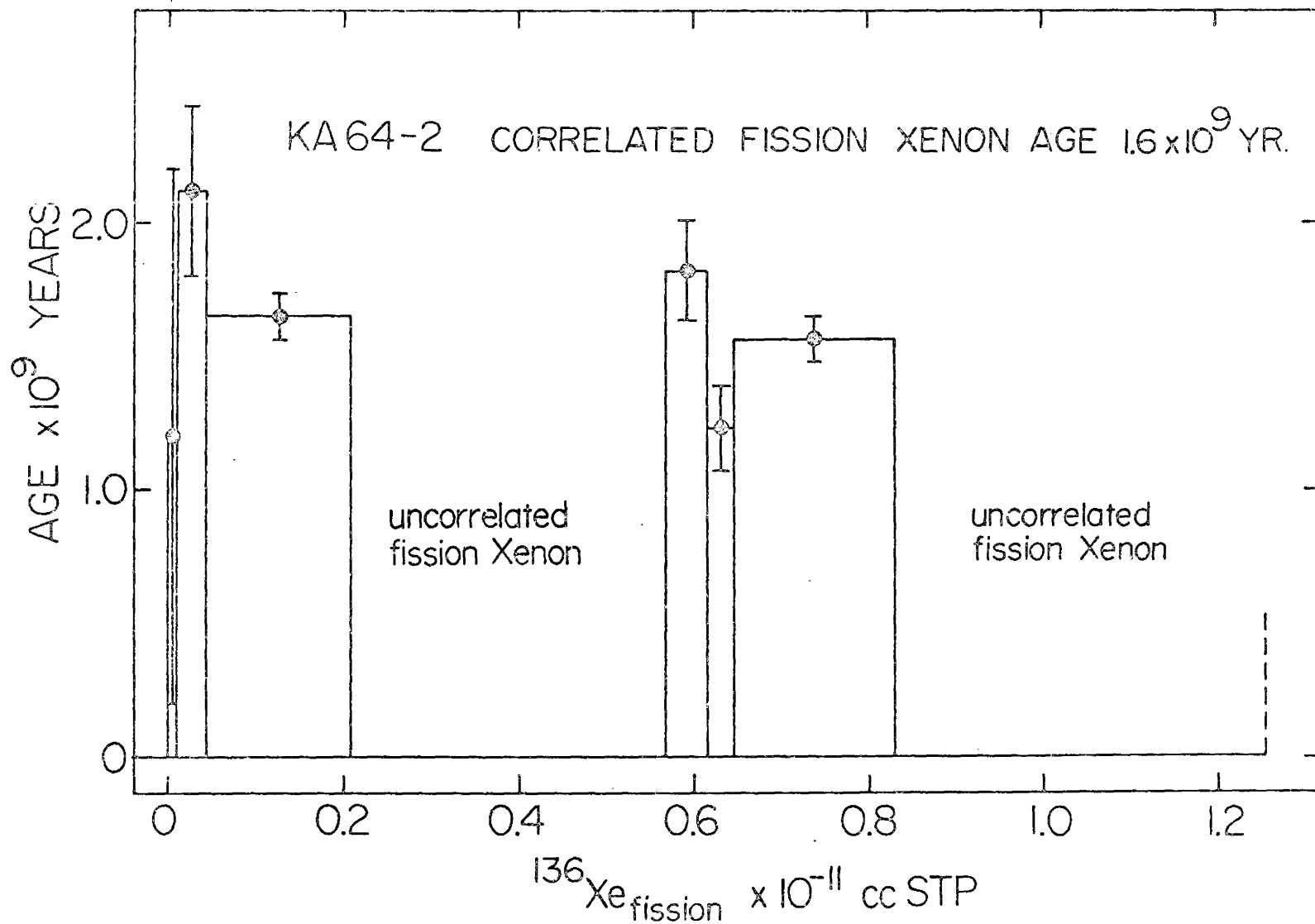


Figure 9 shows the plot of fission xenon dates versus the cumulative amount of fission  $^{136}\text{Xe}$  released. A noticeable difference between this plot and the zircon plots is the relatively large amounts of fission xenon released at lower temperatures compared to those at high temperatures.

The two samples which were not successfully dated were St. Paul's Rocks NE - 4 and Gill nepheline. As mentioned (section A), a subsequent extraction showed that the St. Paul's Rocks sample contained no significant amount of spontaneous fission xenon. In the case of the nepheline sample although fission xenon was observed the amount released was too small to warrant a complete analysis.

## CHAPTER 5

### DISCUSSION

#### A. General Interpretation of the Zircon Data

In the course of the development of the U - Th - Pb dating of zircons it has been shown that generally uranium in zircons is distributed uniformly and is immobile so that in most samples discordancy is caused by Pb loss (Doe, 1970). An exception to this occurs when uranium is added to a zircon during a disturbance in which case the additional uranium is concentrated near the surface of the zircon, and discordancy is the result of both lead loss and uranium gain (Davis et al. 1968).

The fission xenon dating results can be interpreted in a similar manner, i.e. mainly in terms of the diffusion of fission xenon and its precursors. A further aid in interpretation is that as a consequence of the high uranium content of zircon a source of fission xenon other than the uranium in the zircon itself is unlikely. For example, the unlikeliness of extraneous sources plus the low mobility of xenon released at high temperatures led to the criterion that for undisturbed zircon the whole sample age should equal the high temperature plateau age.

Although the whole sample age appears to be

slightly higher than the high temperature plateau age, the fission xenon dating results for sample K 710 (figure 5 and table 6) indicate that it is the least disturbed of the zircon samples<sup>†</sup>. The excess spontaneous fission xenon found in the lowest two temperature fractions of this sample as well as the charnockite sample (figure 7) suggests that during a disturbance xenon drifts to less retentive sites. A similar effect can be expected in undisturbed zircons as a result of fission track damage but the whole sample age and high temperature plateau age should not be significantly affected since the amount of xenon involved should be much smaller.

The pattern of dates (samples K 710, G 2 and charnockite, figures 5, 6, and 7) obtained from xenon evolved between 500°C and 950°C shows a partial breakdown in this temperature range of the assumption that the spontaneous fission xenon release and neutron fission xenon release are correlated. Thus, though the similarity among the patterns (note especially figures 5 and 7) allows an estimate of the date, as is the case in  $^{40}\text{Ar} - ^{39}\text{Ar}$  dating (Brereton, 1972), information obtained in this temperature

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<sup>†</sup> Microscopic examination of the sample also indicated some disturbance. About 10% of the zircons showed overgrowth. In 5% of the grains with overgrowth the overgrowth is overgrowth material (H. P. Schwarcz, private communication).



range should be treated with caution. Specifically it appears that neutron fission xenon is released more readily than spontaneous fission xenon. Two possible explanations are offered. First, the fission tracks from neutron induced fission in a sample are very recent compared to the spontaneous fission tracks. Since fission track studies (Fleischer et al. 1964) have shown that fission tracks anneal with time, the type of site from which xenon is released at these temperatures may be more retentive for spontaneous fission xenon than neutron fission xenon. Second, the precursor diffusion mechanism (see chapter 3, p. 25) may cause lower temperature release of neutron fission  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$  and  $^{133}\text{Xe}$ . If this is the case the intermediate fractions might be interpreted precisely by solving the diffusion problem, but this is difficult and has not been attempted in this thesis.

Neutron fission xenon release was found to be correlated with spontaneous fission xenon release for all four zircon samples, at extraction temperatures greater than  $950^{\circ}\text{C}$ . For each of the samples charnockite and G 2 this is clearly shown by the good agreement among the three highest temperature dates (see figures 6 and 7 and tables 7 and 8).

For all samples this is indicated by the improved agreement among the paired isotope dates (tables 5 to 8).

B. The Western Ahaggar Samples, M 4082 and L - 6

The samples L - 6 and M 4082 came from the Western Ahaggar region in the central Sahara (see figure 10).

Interest in this area was stimulated by efforts to delimit the eastern boundary of the West African craton (Ferrara and Gravelle, 1966). The geochronology of this area as established by the Rb - Sr, K - Ar and U - Th - Pb dating methods has been summarized by Allègre and Caby (1972).

Briefly: Primary deposition occurred between 3.3 by. and 2.8 by. The Suggarien orogeny affected this area between 2.09 by. and 1.96 by. and was responsible for establishing the metamorphic Tassendjanet series and metamorphism and granitization in the In Ouzzal formation. No important tectono-metamorphic event affected this area between 1.96 by. and 0.64 by. although events at 1.1 by. and 1.3 by. have been dated. The Pharusien orogeny (which did not affect the In Ouzzal formation) lasted from 0.64 by. to 0.58 by. and was followed shortly thereafter by the emplacement of the In Zize rhyolites dated at 0.53 by. Phenomena of undetermined nature and weak intensity have

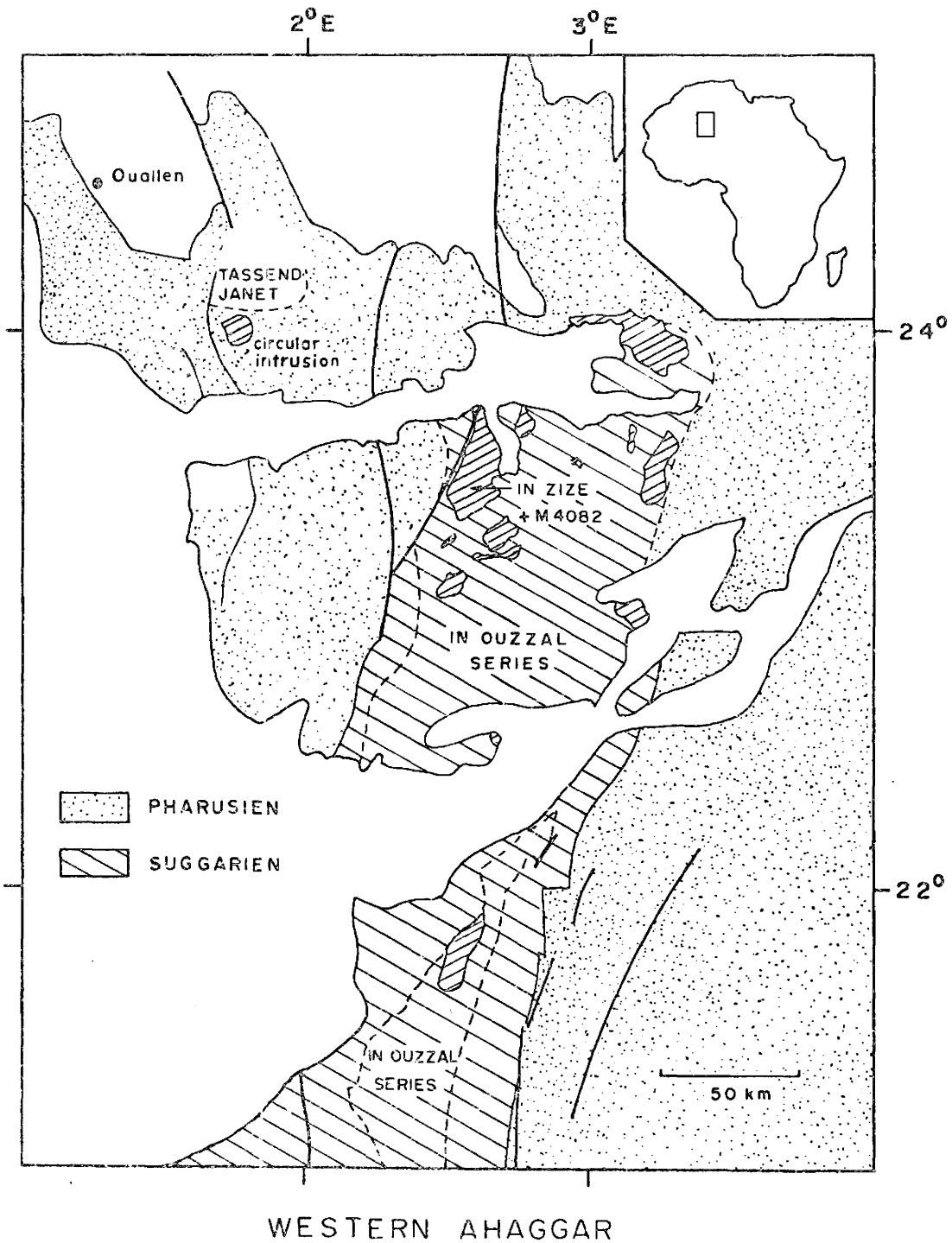


Figure 10. The Western Ahaggar Region. Redrawn from maps by M. Lelubre (Ferrara and Gravelle, 1966), P. Giraud, and R. Cabu (transmitted by C. J. Allègre).

affected this area since 0.45 by..

Sample M 4082 (see figure 4, and table 5) was extracted from charnockitic paragneiss of the In Ouzzal formation and is the first of 3 examples of disturbed zircon. Microscopic examination revealed that this sample is a mixture of two distinct populations of zircon. The zircons of one group are brown, round, detrital and contain black inclusions. The second group consists of well crystalized yellow zircons (Lancelot et al., 1973).

The high temperature plateau date,  $2.82 \pm 0.08$  by., is entirely consistent with the Rb - Sr isochron date, 2.86 by. (Ferrara and Gravelle, 1966) and single zircon analysis (Lancelot et al., 1973). Fission xenon dating appears to have some advantage over the usual U - Th - Pb method since experiments using aggregates of  $\sim 10^4$  zircons resulted in a U - Th - Pb date of 2.17 by. (Allegre et al., 1972) which agrees neither with the age of metamorphism nor with the age of primary deposition. A higher date was obtained by the U - Th - Pb method only when the zircons were analyzed in a single grain at a time.

Fission xenon dating of the low temperature fractions of M 4082 resulted in  $\sim 0$  by. dates (i.e. no

significant spontaneous fission xenon component), in marked contrast with the high dates (excess spontaneous fission xenon) obtained at these temperatures from the disturbed samples, charnockite and G 2, and sample K 710. U - Th - Pb dating of zircon aggregates similarly resulted in a zero date intercept with the concordia curve (concordia curve: see Wetherill, 1956a and 1956b) while grain by grain analysis indicates a recent phenomena (Lancelot et al., 1973). The cumulative amount of fission xenon released below  $650^{\circ}\text{C}$ ,  $\sim 10\%$ , represents the largest fraction of fission xenon released at low temperatures for the zircon samples.

The lack of spontaneous fission xenon in the low temperature fractions of this sample contrasted with the excess spontaneous fission xenon found in the low temperature fractions of the other zircon samples, the relatively large amounts of fission xenon released at low temperatures compared to the total amount released, as well as large radiogenic lead losses indicated by U - Th - Pb analyses, suggest that the 0 by. disturbed age is the result of spontaneous fission xenon loss. The detrital nature of the brown population zircons implies an increased number of unretentive sites and large diffusion coefficients which would facilitate both xenon and lead loss. Assuming

episodal loss the results indicate a recent alteration. On the other hand detrition indicates the possibility of continuous diffusion losses. If this is the case, M 4082 may provide an excellent sample for testing continuous diffusion lead loss theories.

The age plateau obtained from xenon released between  $650^{\circ}\text{C}$  and  $1100^{\circ}\text{C}$  possibly shows a second disturbance since the dates from which it was derived do not appear to be associated with either the high or low temperature plateau dates. But the plateau is not well defined and as mentioned previously results obtained in this temperature range cannot be interpreted precisely. If confirmed, this result might be the first indication that the Pharusien orogeny affected the In Ouzzal formation.

The whole sample age,  $2.98 \pm 0.12$  by., of sample L - 6 collected from Tassendjanet is the only example of serious disagreement between the fission xenon dating method and the U - Th - Pb and Rb - Sr methods. The latter methods date this complex at 1.96 by. - 2.09 by. Unfortunately the amount of the sample available was too small to permit a stepwise heating experiment. The excellent agreement between the least squares fit date and the paired

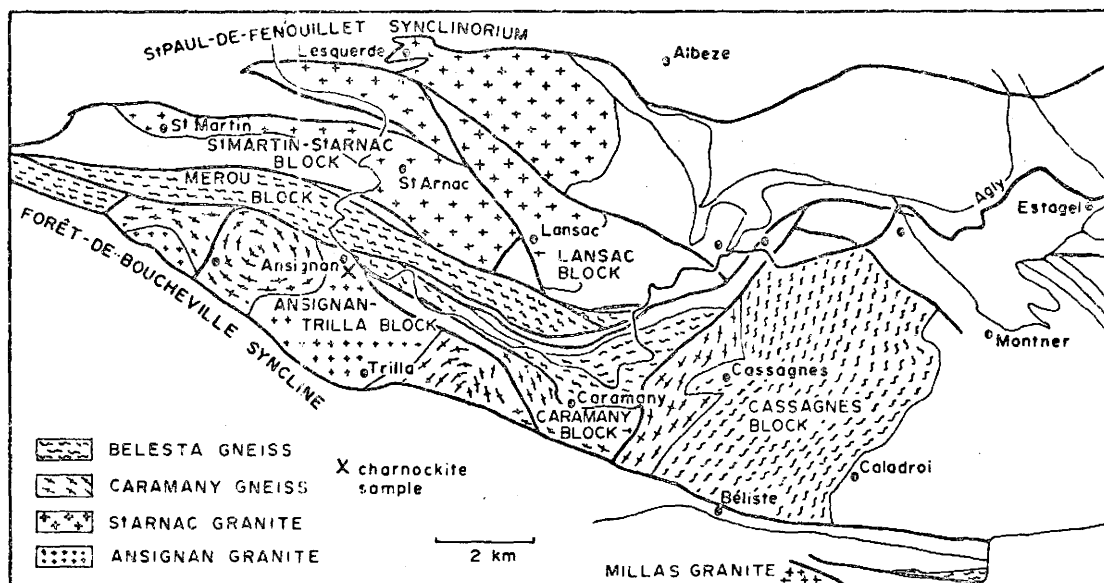
isotope dates (see table 4) indicates a valid age determination but without further information the discrepancy between fission xenon method and the other methods must remain unresolved.

C. The Eastern Pyrenees Samples, Charnockite and G 2

In the eastern Pyrenees, each surrounded by secondary terrain, the two massifs, Agly and Canigou, are surface features of older material underlying the Pyrenees. Samples from them can thus be used to investigate the geochronology of the two major episodes known to have affected this area prior to the formation of the present day Pyrenees.

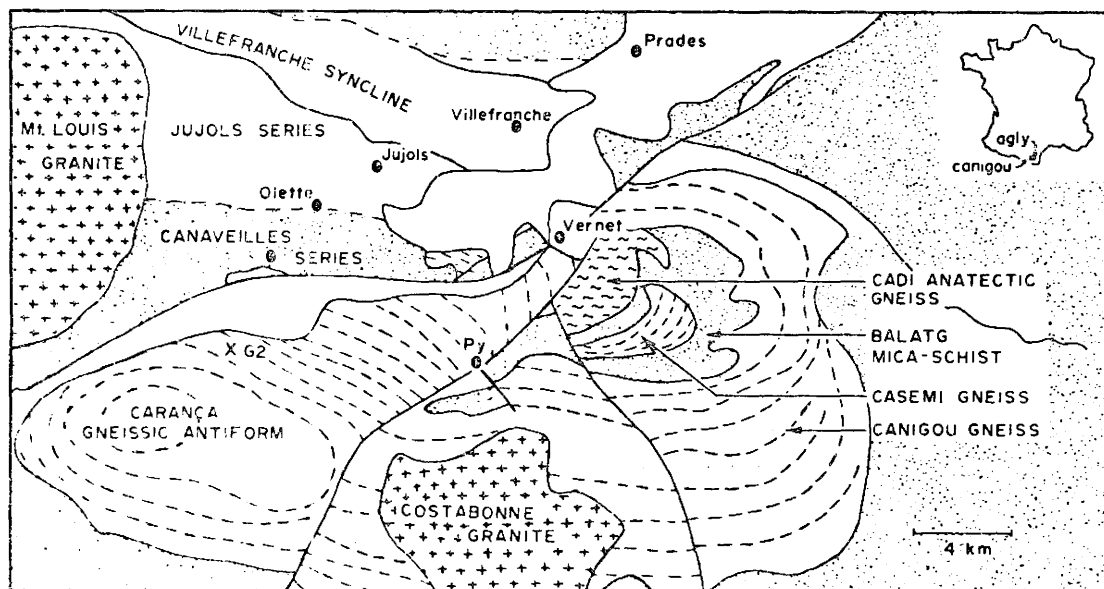
The charnockite zircons were extracted from charnockite granite (Ansignan granite) from the Agly massif. Microscopic examination of the sample revealed clear well crystallized zircons. Previous dating of this granite by the U - Pb and Rb - Sr techniques gave the following results:

(a) A U - Pb date of about 0.30 by., based on the estimate that a plot of the results from slightly discordant zircons (disturbed by the Pyrenees orogeny, 0.11 by. to 0.045 by.) intercepted the concordia curve at the date given by the concordant age obtained from a sample of monazite (Vitrac, 1972).



### AGLY MASSIF

(redrawn from a map transmitted by C. J. Allègre)



### CANIGOU MASSIF

(after P. Guitard; transmitted by C. J. Allègre)

Figure 11. The Canigou and Agly Massifs in the Eastern Pyrenees



(b) Rb - Sr analyses of this granite showed that the results fitted the 0.580 by. isochron obtained from the Rb - Sr analyses of Caramany charnockitic gneiss<sup>†</sup> (Vitrac and Allègre, 1971).

Based on the appearance of the zircons, the U - Pb results which gave no indication of an earlier event, and the uniformity of strontium isotope ratios indicating almost complete homogenization, fission xenon dating was expected to show an undisturbed age of about 0.3 by. The xenon results therefore were somewhat startling.

Figure 6 shows that the high temperature plateau age,  $0.353 \pm 0.024$  by., corresponding to the expected Hercynien (0.33 by. to 0.28 by.) age, is slightly too high and that large amounts of excess spontaneous fission xenon were released from the sample at temperatures less than  $950^{\circ}\text{C}$ . The whole sample age,  $0.589 \pm 0.049$  by. (table 7) in fact agrees not with the expected date but with the older Rb - Sr isochron age of the charnockite gneiss.

---

<sup>†</sup> The purpose of this was to show that this granite was not of juvenile origin but was the result of anatexis of the charnockites. The fission xenon dating results furnish a direct proof.

These results clearly show that the zircons were inherited and thus they confirm the indication obtained from the Rb - Sr results that the granite is not of juvenile origin. They also show that disturbance in this case caused a redistribution of xenon within the zircons, but of greater importance they show that even a severe disturbance does not necessarily cause complete loss of spontaneous fission xenon. In terms of the ability of a dating method to see past a metamorphic event these results indicate that fission xenon dating is better able to do this than other methods.

The results from zircon sample G 2 were less exciting. The zircons were separated from gneiss (sample G 2 J) from the Canigou massif (see figure 11). Microscopic examination revealed that these zircons also were clear and well crystalized. Previous dating of various gneiss samples from the Canigou massif including G 2 J showed that the results fit a 0.550 by. Rb - Sr isochron (Vitrac and Allegre, 1971). Granite from this massif also dated by the Rb - Sr isochron technique was found to be  $0.330 \pm 0.010$  by. old (Vitrac and Allègre, 1973). U - Pb dating of the G 2 zircons showed that they were discordant. Extrapolation of the data resulted in intercepts

with the concordia curve at 0.29 by. and 0.62 by.

(Allègre, private communication).

Fission xenon dating of this sample (see figure 7 and table 8) resulted in a high temperature plateau age of  $0.434 \pm 0.020$  by. and a whole sample age of  $0.432 \pm 0.031$  by.. This age, intermediate between the date of the Precambrian and Hercynien episodes, corresponds to the date indicated by the mean position of the zircon results on the concordia plot implying that disturbance in this case affected the U - Xe and U - Pb systems in a similar manner. The effect of disturbance on the U - Xe system is not clear. Addition of fresh material seems unlikely since only a single zircon out of about one hundred showed an overgrowth. Xenon loss is also not likely because of the exact agreement between the whole sample age and the high temperature plateau age. The intermediate age may be the result from a mixed population of zircons, but if so the populations are apparently indistinguishable by microscopic examination.

#### D. Normal Rock Samples

The nepheline results showed that a fission xenon date of sufficient precision (error < 10%) can be obtained

from this sample provided a 10 gm quantity is used. Unfortunately, the capacity of the extraction apparatus was insufficient at the time of the experiments to handle a sample of that size. Figure 12 shows that the amount of excess spontaneous fission xenon in this sample is about the same as that of other normal uranium content rock samples in which spontaneous fission xenon was detected. Thus the fission xenon dating method could be used to date a large fraction of normal uranium content rock samples. It must be cautioned however that this involves quantities of fission xenon of the order of  $10^{-12}$  cc STP  $\text{gm}^{-1}$  in the presence of large atmospheric components and thus requires instrumentation of the highest sensitivity and precision.

Carbonatite KA 64-2 was obtained from the Visser Kimberlite pipe in Tanganyika. Its chief attraction as far as the fission xenon dating method was concerned, was the large excess of spontaneous fission xenon observed (see table 1).

The graph of the age versus the cumulative amount of fission  $^{136}\text{Xe}$  released shows a mean age of  $1.6 \pm 0.2$  by., in reasonable agreement with early experiments carried out by the author which resulted in a  $^{136}\text{Xe}/^{129}\text{Xe}$  versus

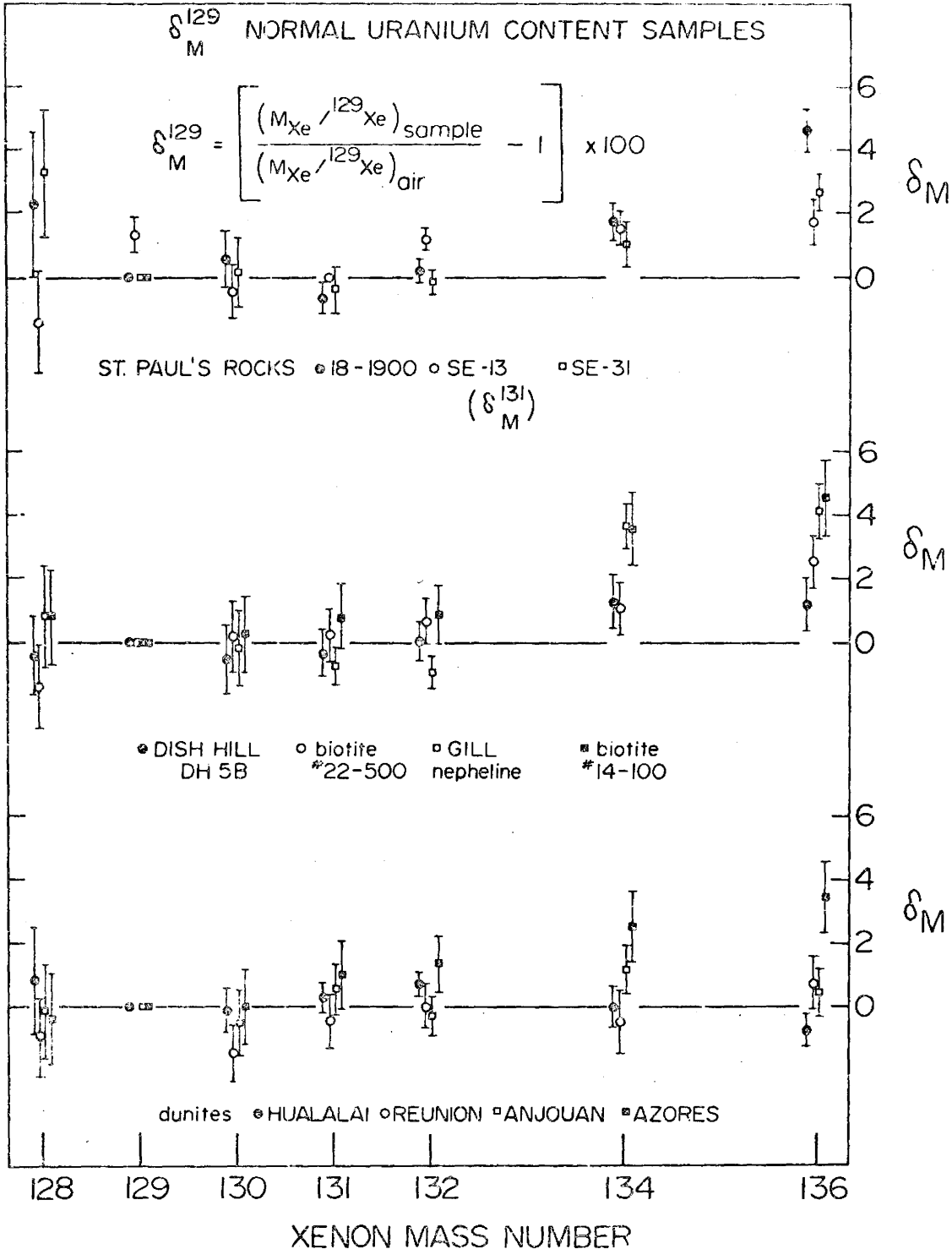


Figure 12. The relative spontaneous fission product xenon abundance of normal uranium content samples. Spontaneous fission xenon is indicated by  $\delta_M^{129}$  values greater than zero for masses 136, 134, 132, and 131.

$^{134}\text{Xe}/^{129}\text{Xe}$  isochron age for this sample of 1.1 by.,

In addition to the fission xenon used to obtain this date, large amounts of uncorrelated fractionated spontaneous fission were released in the  $650^{\circ}\text{C} - 800^{\circ}\text{C}$  (corresponding to the decomposition of  $\text{CaCO}_3$ ) and the  $1250^{\circ}\text{C} - 1400^{\circ}\text{C}$  heating steps. At present the interpretation is that the uranium in the sample is the source of this spontaneous fission xenon. A second unusual feature of this sample is excess  $^{130}\text{Xe}$  which was clearly present in the high temperature fractions ( $650^{\circ}\text{C} - 1400^{\circ}\text{C}$ ). The assumption that the excess  $^{130}\text{Xe}$  is the result of double beta decay of  $^{130}\text{Te}$  ( $T_{1/2} = 8 \times 10^{20}$  yr.) results in a  $^{130}\text{Xe}/^{129}\text{Xe}$  versus  $^{131}\text{Xe}$  excess/ $^{129}\text{Xe}$  isochron date of  $11 \pm 5$  by..

Although the uranium content of this sample, 2.8 ppm (W. B. Clarke, private communication), is low enough, the unusual nature of this sample makes it unrepresentative of a typical normal uranium content sample. The ability of the fission xenon method to date normal uranium content samples is therefore better demonstrated by the nepheline results.

## E. Miscellaneous

### 1. Calibration by a Standard of Known Age

In the present work 1% Co - Al wires were used to measure the neutron flux without a calibration by means of a standard of known age. This method has been shown to be adequate. However this requires control of the irradiation, and familiarity with irradiation techniques. When either of these conditions is not met, the 1% Co - Al monitors are best calibrated for a particular irradiation facility by a sample of known age. Once a facility has been calibrated the neutron flux can be measured exclusively by the use of 1% Co - Al flux monitors.

### 2. Optimization of the Irradiation Time

By noting that  $K/N$  in equation ( 4 ), p. 39 is a constant it is apparent that the error in a date is minimized by minimizing the quantity.

$$\frac{\sigma_s^2}{s^2} + \frac{\sigma_N^2}{N^2}$$

The results show that the error in the neutron fission component is approximately  $2/3$  that of the spontaneous

fission component. Further, it can be reasonably assumed that  $\sigma_s^2$  is proportional to  $Y_S S + Y_N N + Y_A A$  where  $Y_S$ ,  $Y_N$ , and  $Y_A$  are respectively the sum of the spontaneous fission, neutron fission and air yields. The optimization equation therefore is

$$\left(\frac{N}{S}\right)^2 = \frac{4}{9} \left[ \frac{2 \left( \frac{Y_S}{Y_N} S + \frac{Y_A}{Y_N} A \right) + 1}{N} \right]$$

In the simplest case, neglecting the air component and setting  $Y_S = Y_N$ , iteration shows that the error in a date is minimized by irradiating a sample so that  $N/S$  is about 1.1 .



## CHAPTER 6

### CONCLUSION

The fission xenon dating method as set out in the present work has been shown to be superior to other methods in some cases. This was first demonstrated by the results of sample M 4082, and shown in an impressive manner by the charnockite results. In both cases the fission xenon dating method extracted in a single experiment from a single sample information which had previously required the use of several techniques and many samples. In this respect, the value of the stepwise degassing technique used in conjunction with the new method cannot be overemphasized. This was made clear by the results from sample L - 6 for which the disagreement between the date obtained and the accepted date could not be resolved because of a lack of information.

The use of many isotopes has been shown to have advantages: the precision and reliability are increased by averaging up to four dates while simultaneously estimating the atmospheric correction by as many as six isotopes, the

degree of correlation between the release of neutron and spontaneous fission xenon can be assessed from the agreement among the paired isotope dates, and the excess abundance of an isotope is more apparent. But the mass spectrometry and the subsequent analysis are time consuming to an extent not always warranted. The measurement of fewer isotopes greatly reduces the effort required to date a sample. The results show that amongst the simplest versions of the method the highest precision is obtained from the triplet  $^{136}\text{Xe}$ ,  $^{133}\text{Xe}$  and  $^{129}\text{Xe}$ .  $^{134}\text{Xe}$  can be substituted for either of the fission isotopes in the triplet, though if substituted for  $^{133}\text{Xe}$  the precision is reduced substantially. As an addition to  $^{136}\text{Xe}$  and  $^{133}\text{Xe}$  in a three fission isotope method, the choice is between  $^{134}\text{Xe}$  and  $^{132}\text{Xe}$ .  $^{134}\text{Xe}$  has the advantage since the  $^{134}\text{Xe}/^{133}\text{Xe}$  and  $^{134}\text{Xe}/^{136}\text{Xe}$  dates are respectively more precise than the  $^{132}\text{Xe}/^{133}\text{Xe}$  and  $^{132}\text{Xe}/^{136}\text{Xe}$  dates,  $^{134}\text{Xe}$  next to  $^{136}\text{Xe}$  is least affected by precursor diffusion, and it is an insurance isotope because it does not decay and can be substituted for  $^{133}\text{Xe}$  (e.g. sample KA 64 - 2).  $^{132}\text{Xe}$  used as a third fission isotope, reduces the error in the air component determination or indicates the severity of the precursor diffusion effect. Based on the results, for

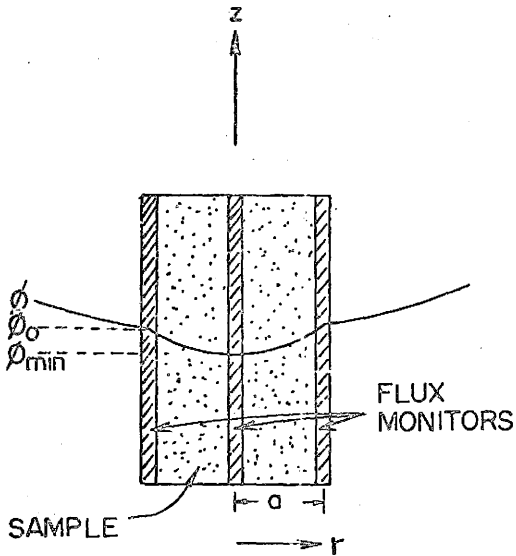
high uranium content samples, the use of  $^{131}\text{Xe}$ , except when all seven isotopes are used, cannot be recommended when the extraction temperatures are less than  $1400^{\circ}\text{C}$  since the measurement of its abundance is too severely affected by precursor diffusion. It is not a useful isotope for normal uranium content samples (e.g.

KA 64 - 2) because it is the product of neutron capture by  $^{130}\text{Te}$  and  $^{130}\text{Ba}$ . The isotope,  $^{130}\text{Xe}$ , should be used in addition to  $^{129}\text{Xe}$  if due to a very high uranium content, neutron fission has occurred in a sample prior to irradiation.

In the introduction two criteria were set out for judging the value of a new technique, namely, it should provide additional information, and it should not be too difficult experimentally. The fission xenon dating method has been shown to provide extra information by two examples. Its simple version, the  $^{136}\text{Xe} - ^{133}\text{Xe}$  technique, while retaining many of the advantages of the complete method, is not difficult experimentally.

## APPENDIX 1

### Flux Depression Correction (Cylindrical Samples)



Neutron flux monitors extending the length of a sample inherently measure the flux averaged over the length ( $z$  direction) of the sample. In the radial direction the solution of the neutron diffusion equation (Glasstone 1952, p.106) yields the relation  $\phi(r) = \phi_{\min} I_0(kr)$  (see figure) where  $I_0$  is the modified

Bessel function and  $k$  is essentially a scaling factor. Using the relation

$$\int_0^z t^\nu I_{\nu-1}(t) dt = z^\nu I_\nu(z) \quad (\text{Abramowitz 1968})$$

the average neutron flux is given by the expression

$$\bar{\phi} = \frac{2I_1(ka)}{ka} \phi_{\min}$$

where  $ka$  is determined from the equation

$$I_0(ka) = \phi_0 / \phi_{\min}$$

Practically,  $I_0(ka)$  may be replaced by the parabolic approximation,  $1 + (k' a)^2$ , yielding

$$\bar{\phi} = 1 + \frac{(k' a)^2}{2} \phi_{\min.}$$

where

$$(k' a)^2 = \phi_0 / \phi_{\min.} - 1$$

For a flux depression as large as 10% this approximation results in an error of only 0.04% in the average flux.



where

$Y_N$  = the absolute chain yield

$I_i$  = the fractional independent yield of the  
 $i^{\text{th}}$  member

and

$\sigma_{235}$  = neutron fission cross section of  $^{235}\text{U}$ .

The solutions of these equations may be obtained either by the method of Bateman (1910) or that described by Kaplan (1962)<sup>†</sup> and result in relations of the form

$$\begin{aligned}
 N_i = & \text{first term} + F_{i-1} \left[ \frac{e^{-\lambda_i t}}{(\lambda_{i-1} - \lambda_i)} + \frac{e^{-\lambda_{i-1} t}}{(\lambda_i - \lambda_{i-1})} \right] \\
 & + F_{i-2} \lambda_{i-1} \left[ \frac{e^{-\lambda_i t}}{(\lambda_{i-1} - \lambda_i)(\lambda_{i-2} - \lambda_i)} + \frac{e^{-\lambda_{i-1} t}}{(\lambda_i - \lambda_{i-1})(\lambda_{i-2} - \lambda_{i-1})} + \frac{e^{-\lambda_{i-2} t}}{(\lambda_i - \lambda_{i-2})(\lambda_{i-1} - \lambda_{i-2})} \right] \\
 & + \dots + F_i \lambda_1 \lambda_2 \dots \lambda_{i-1} \left[ \frac{e^{-\lambda_i t}}{(\lambda_{i-1} - \lambda_i)(\lambda_{i-2} - \lambda_i) \dots (\lambda_1 - \lambda_i)} + \dots + \frac{e^{-\lambda_1 t}}{(\lambda_i - \lambda_1)(\lambda_{i-1} - \lambda_1) \dots (\lambda_2 - \lambda_1)} \right]
 \end{aligned}$$

---

<sup>†</sup> The  $i^{\text{th}}$  equation is solved by multiplying by the integrating factor  $e^{\lambda_i t}$ , rearranging the equation to form

$$\frac{dN_i e^{\lambda_i t}}{dt} = P_i e^{\lambda_i t} + \lambda_{i-1} N_{i-1} e^{\lambda_i t} \quad \text{and}$$

integrating after substituting for  $N_{i-1}$  the expression found for  $N_{i-1}$  by solving for the  $(i-1)^{\text{th}}$  equation.

where a) during irradiation if the  $i^{\text{th}}$  member is

unstable the first term =

$$\frac{P_1 + P_2 + \dots + P_i}{\lambda_i} [1 - e^{-\lambda_i t}] \text{ and}$$

$$F_j = - (P_1 + P_2 + \dots + P_j)$$

b) during irradiation if the  $i^{\text{th}}$  element is

stable the first term =

$$(P_1 + P_2 + \dots + P_i)t \text{ and}$$

$$F_j = - (P_1 + P_2 + \dots + P_j)$$

c) after irradiation (i.e.  $P_1 = P_2 = \dots = P_i = \dots = 0$ )

let the abundances at the end of an irradiation

of duration  $T$  be  $N_1(T)$  ,  $N_2(T)$  ,  $\dots$  ,  $N_i(T)$  ,  $\dots$

(calculated using the above expressions) and let

$t'$  be the time measured from the end of the

irradiation (i.e.  $t' = t - T$ ) then  $t'$  is

substituted for  $t$ , the first term =  $N_i(T)e^{-\lambda_i t'}$

and  $F_j = + N_j(T)\lambda_j$ .

In this case the expressions for  $F_j$  and the first

term hold whether the  $i^{\text{th}}$  element is stable or

unstable. In practice, when a chain contains more

than two or three members, the computations should

be done by computer, or appropriate approximations

(e.g. Macnamara (1950) or Katcoff (1953)) made to

reduce the length of the chain.



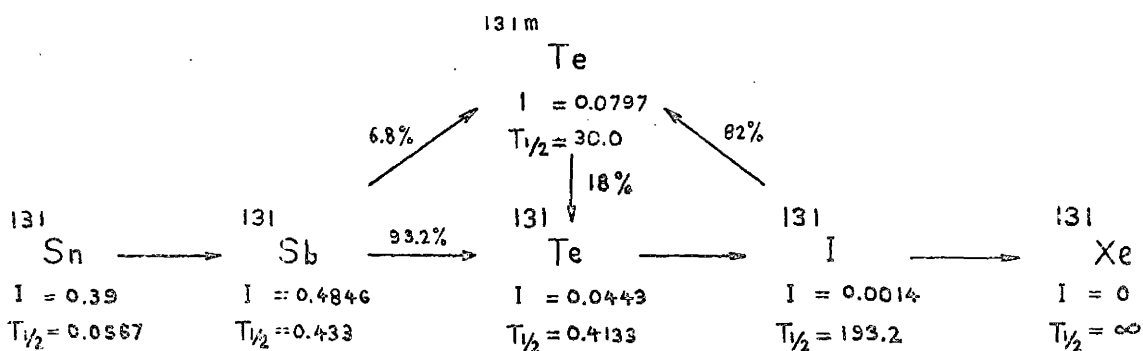
B. The Decay Chains for Masses 131, 132 and 133.

In the case of fission xenon dating the equations given in part A are applied when calculating the fractions of the fission chain yields present as  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ , and  $^{133}\text{Xe}$  at the time of mass spectrometric analysis. The information required in the calculations is given in the decay chains shown below and was gathered from the following sources.

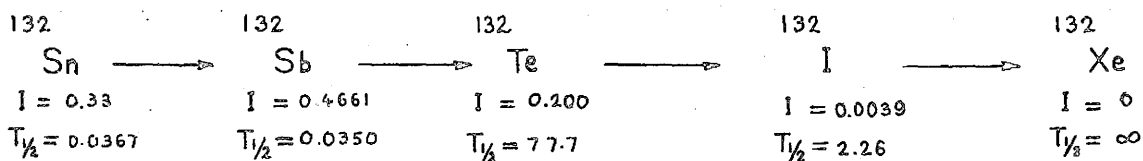
- half lives and branching ratios from Lederer (1968)
- fractional independent fission yields,  $I$ , from Wahl (1969)
- the ratios  $I(^{131\text{m}}\text{Te})/I(^{131}\text{Te}) = 1.8$  and  $I(^{133\text{m}}\text{Te})/I(^{133}\text{Te}) = 1.55$  from Sarantites (1965)
- the ratio  $I(^{133\text{m}}\text{Xe})/I(^{133}\text{Xe})$  was assumed to be 1.5

The decay chains are:

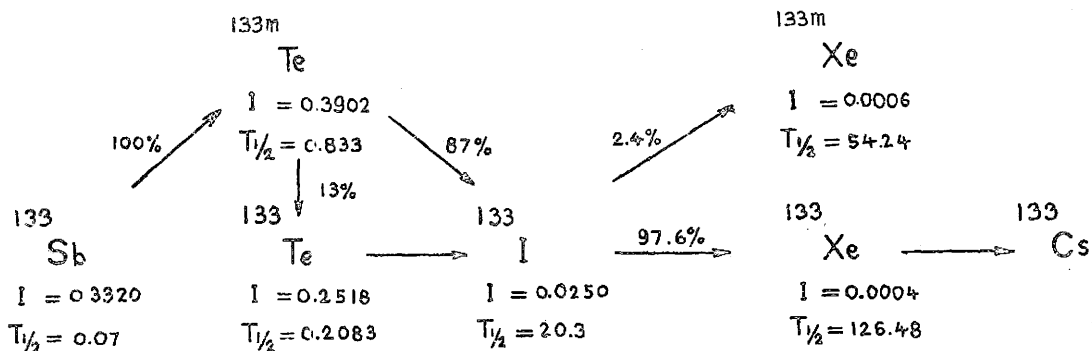
Mass 131



## Mass 132



## Mass 133



Complex decay chains are best treated as the sum of independent decay chains (for an example see Appendix III). Since only the fractions of the chain yields observed at the time of analysis are required, the calculations of the abundances are normalized so that after an infinite decay time the yield of the last, stable, member of a chain is unity.

APPENDIX III

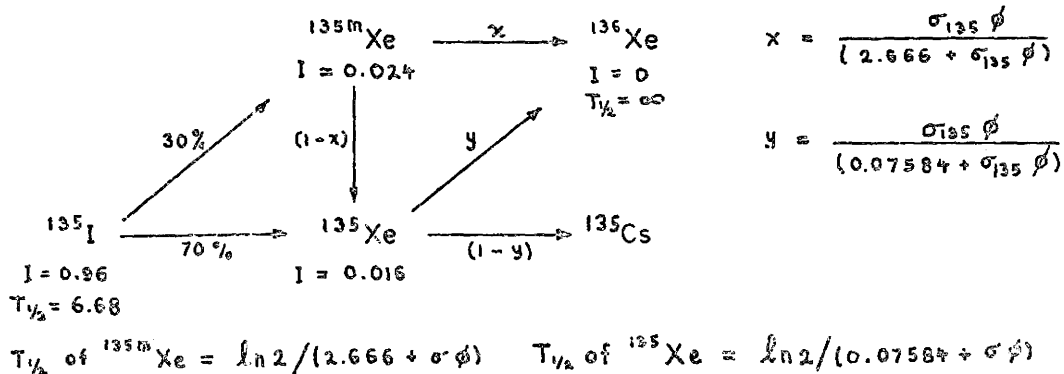
The  $^{135}\text{Xe}(n,\gamma)^{136}\text{Xe}$  Correction to  $Y_N^{136}$

Neutron capture during irradiation is described by differential equations of the form

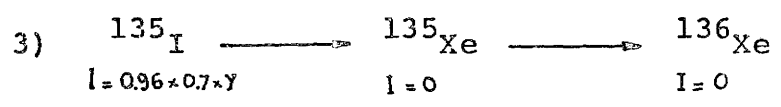
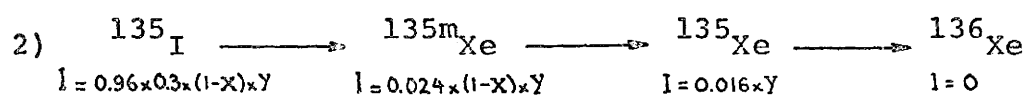
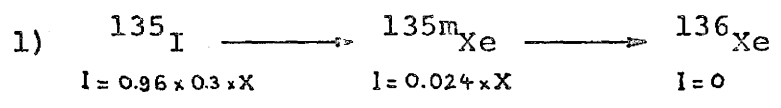
$$\frac{dN}{dt} = P + \lambda(^{135}\text{I})N(^{135}\text{I}) - \lambda N - \sigma\phi N$$

for  $^{135}\text{Xe}$  and  $^{135m}\text{Xe}$ . From this expression it can be seen that the neutron capture contribution can be accounted for by the use of an effective decay constant  $\lambda' = \lambda + \sigma\phi$ , and by using the branching fractions  $\frac{\lambda}{\lambda'}$ , for decay to the next member of the decay chain, and  $\frac{\sigma\phi}{\lambda'}$  for neutron capture to  $^{136}\text{Xe}$ .

Using the references given in Appendix II and the assumptions  $I(^{135m}\text{Xe})/I(^{135}\text{Xe}) = 1.5$ , and  $\sigma_{135} = 3.6 \times 10^6$  barns for both  $^{135m}\text{Xe}$  and  $^{135}\text{Xe}$ , the mass 135 decay chain including neutron capture is



This chain can be split up into five independent chains of which the following three chains contribute to  $Y_N^{136}$  :



The fraction of the mass 135 chain transformed to  ${}^{136}\text{Xe}$  is calculated using the equations developed in Appendix II. The contribution to  $Y_N^{136}$  is then this fraction times the absolute fission chain yield of the mass 135 chain.

#### APPENDIX IV

### Least Squares Analysis of an Isotopic Composition

Let  $R_i$  be the measured isotopic abundance of isotope  $i$ ,  $w_i$  be the statistical weight of  $R_i$ , and  $Y_N^i, Y_S^i, \dots, Y_A^i$  be the yields of components N, S, ..., A. Then using the method of least squares, the minimization of the weighted sum of the squares of the deviations,

$$M = \sum_i [R_i - (Y_N^i N + Y_S^i S + \dots + Y_A^i A)]^2 w_i$$

results in the normal equations

$$N \sum_i Y_N^i Y_N^i w_i + S \sum_i Y_S^i Y_N^i w_i + \dots + A \sum_i Y_A^i Y_N^i w_i = \sum_i R_i Y_N^i w_i$$

$$N \sum_i Y_N^i Y_S^i w_i + S \sum_i Y_S^i Y_S^i w_i + \dots + A \sum_i Y_A^i Y_S^i w_i = \sum_i R_i Y_S^i w_i$$

$$\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots$$

$$N \sum_i Y_N^i Y_A^i w_i + S \sum_i Y_S^i Y_A^i w_i + \dots + A \sum_i Y_A^i Y_A^i w_i = \sum_i R_i Y_A^i w_i$$

This set of equations may be solved for the components, N, S, ..., A, either by the use of determinants or by matrix inversion. In the latter case the normal equations are expressed as

$$Y = C R$$

where

$$Y = \begin{vmatrix} \sum_i Y_N^i Y_N^i w_i & \sum_i Y_S^i Y_N^i w_i & \cdots & \sum_i Y_A^i Y_N^i w_i \\ \sum_i Y_N^i Y_S^i w_i & \sum_i Y_S^i Y_S^i w_i & \cdots & \sum_i Y_A^i Y_S^i w_i \\ \vdots & \vdots & \ddots & \vdots \\ \sum_i Y_N^i Y_A^i w_i & \sum_i Y_S^i Y_A^i w_i & \cdots & \sum_i Y_A^i Y_A^i w_i \end{vmatrix}$$

$$C = \begin{vmatrix} N \\ S \\ \vdots \\ A \end{vmatrix} \quad R = \begin{vmatrix} \sum_i R_i Y_N^i w_i \\ \sum_i R_i Y_S^i w_i \\ \vdots \\ \sum_i R_i Y_A^i w_i \end{vmatrix}$$

and the solution is

$$C = Y^{-1} R$$

where  $Y^{-1}$  is the inverse of  $Y$ .

If  $w_i = 1/\sigma_i^2$ , where  $\sigma_i$  is the standard error in  $R_i$ , then  $Y^{-1}$  is the variance-covariance matrix and the variances of the components are the diagonal terms of this matrix. Alternatively the errors may be calculated from the external consistency of the least squares fit by the relation

$$\text{variance-covariance matrix} = Y^{-1} \chi^2$$

where

$$\chi^2 = \frac{M}{N-f}$$

$N$  is the number of isotopes used in the fit and  $f$  is the number of parameters fitted.

The components may be calculated in an equivalent manner using Cramer's Rule. Letting  $D_0 = \text{determinant } |Y|$  and  $D_N, D_S, \dots, D_A$  be the determinants of the matrices formed by substituting  $R$  for the first, second,  $\dots$ , last columns in  $Y$  respectively, the values of the components are given by the equations

$$N = D_N/D_0, S = D_S/D_0, \dots, A = D_A/D_0$$

Using the component,  $N$ , as an example the variances of the components are calculated from equations of the form

$$\sigma_N^2 = \sum_i \left( \frac{\partial N}{\partial R_i} \right)^2 \sigma_i^2$$

where the variances,  $\sigma_i^2$ , are either known from the isotopic abundance measurements, or can be estimated from the formula

$$\sigma_i^2 = \frac{\chi^2}{w_i}$$

and where

$$\frac{\partial N}{\partial R_i} = \frac{1}{D_0} \begin{vmatrix} Y_N^i w_i & \sum_j Y_S^j Y_N^j w_j & \dots & \sum_j Y_A^j Y_N^j w_j \\ Y_S^i w_i & \sum_j Y_S^j Y_S^j w_j & \dots & \sum_j Y_A^j Y_S^j w_j \\ \vdots & \vdots & \ddots & \vdots \\ Y_A^i w_i & \sum_j Y_S^j Y_A^j w_j & \dots & \sum_j Y_A^j Y_A^j w_j \end{vmatrix}$$

As a consequence of the last equation the partial derivatives,  $\frac{\partial S}{\partial R_1}$ ,  $\frac{\partial S}{\partial R_2}$ , ...,  $\frac{\partial A}{\partial R_i}$ , may be evaluated by using the fictitious abundances  $R_i = \delta_{ij}$ , where  $\delta_{ij} = 1$  if  $i = j$  and  $\delta_{ij} = 0$  if  $i \neq j$ .

References:

- Young, chap. 14 and 15 (method of least squares)
- Deming, pp. 156-167 (variance-covariance matrix)
- Bevington, pp. 152-154 (variance-covariance matrix)
- Appendix B (matrix inversion)



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