XENON AND KRYPTON IN PITCHBLENDE AND THE SPONTANEOUS FISSION OF U^{238}

By

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Scope and contents of this thesis:

The mass patterns of the xenon and krypton isotopes extracted from pitchblende samples from the Great Bear Lake region and from the Belgian Congo have been studied using a 180° mass spectrometer. The mass yield curve for the spontaneous fission of U^{238} has been deduced from the xenon and krypton isotope abundance measurements. Differences have been detected in the mass yield patterns for the two ores and their significance is discussed.

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INTRODUCTION

The discovery of fine structure in the mass yield curve[1,2] for neutron fission of U^{235} in the neighbourhood of the 82 neutron shell indicated that the stability of this configuration had an important effect on the mass yield pattern. If the fine structure is produced by the 82 neutron shell and arises at the instant of fission it would occur at the same mass values for any fissioning nucleus. On the other hand if the fine structure arises from branching in the decay chains of the fission products it would probably occur at different mass values for different fissioning nuclei because of the shifting of the primary fission yields. In the case of spontaneous fission, where the nucleus has more time to assume the most favorable configuration before fission takes place, the fine structure might be much more prominent. Because of these facts an accurate determination of the mass yield curve for the spontaneous fission of U^{238} should lead to a better understanding of the fine structure and of the entire fission process.

The spontaneous fission of uranium was discovered in 1940 by Flerov and Petrzahak[3] by the detection of the fission fragments in a large, uranium lined ionization chamber. They estimatedthe half life for spontaneous fission to be 10^{16} to 10^{17} years. Neutrons arising from the spontaneous fission of uranium were detected by Maurer and Pose[4] in 1943 using a large boron counter surrounded by a uranium casing and enclosed in paraffin. Several experiments were carried out to demonstrate that the observed neutrons were not produced by cosmic rays or by (α,n) reactions in the uranium. During the years 1943-49 the spontaneous fission half life was measured by several workers using different methods. Their

TABLE I

WORKERS	HALF LIFE (YEARS)	METHOD OF DETECTION	REFERENCE
Maurer and Pose	$2.0 \times 10^{15} \pm 25\%$ ☆	neutrons-Boron counter	4
Chatterjee	1.3×10^{16}	neutrons-Boron lined BF_3 ionization chamber	5
Klaiber	3.1×10^{15} ☆	neutrons-Hydrogen ionization chamber	6
Perfilov	$1.3 \pm 0.2 \times 10^{16}$	fission fragments-photographic plates	7
Yagoda and Kaplar	$1.9 \pm 0.1 \times 10^{15}$ ☆	neutrons-Boron loaded photographic plates	8
Segre	U_{238} $8.04 \pm 0.3 \times 10^{15}$ U_{235} $1.87 \pm 0.6 \times 10^{17}$	fission fragments Argon ionization chamber	9

results are given in Table I.

The starred values in this table are calculated on the assumption of one neutron per fission and hence can be expected to be low since it is known[10] that for neutron fission of U^{235} the average number of neutrons per fission is 2.5 ± 0.1. The number of neutrons per spontaneous fission was estimated by Chatterjee[5] to be three and has been measured by Segre[9] to be 2.2 ± 0.3.

The work reported by Segre probably represents the best experimental value of the half life available to date and is the only reported work in which the separated isotopes have been studied.

No satisfactory theoretical explanation of spontaneous fission has as yet been found. Attempts to calculate the half life based on the liquid drop model, assumptions of the transparency of the potential barrier, and calculations of the photo fission threshold energy have been made by Bohr and Wheeler[11], Flugge[12], and Turner[13]. The agreement of these results with experiment is very poor. The values calculated by Flugge are: U^{235} - 3×10^{13} years; U^{238} - 3×10^{16} years.

In 1945 the occurence of Pu^{239} in pitchblende ores was reported by Seaborg[14]. The source of this plutonium was considered to be (n, γ) reactions on U^{238}. If the neutron flux in pitchblende is sufficient to produce detectable quantities of plutonium it is reasonable to expect that there has been considerable neutron fission of the uranium isotopes in the pitchblende in addition to the known spontaneous fission.

The work of Thode and Graham[1] had shown that the isotopes of xenon and krypton occur in high yields in neutron fission of U^{235} and that the mass patterns of fission product xenon and krypton are completoly different from those of normal xenon and krypton. For these reasons it was thought that it should be possible to detect the presence of the rare gas fission products in pitchblende even if the ore contained considerable quantities of normal xenon and krypton. Accordingly pitchblende samples were collected in this laboratory in preparation for the extraction of the rare gases. During the course of this work Khlopin, Gerling, and Barnanovskya[15] reported the presence of excess xenon in pitchblende and attributed this to the spontaneous fission of uranium. In a sample of uraninite from Chernaya Sal'ma containing 63% uranium they found, per kilogram of uranium, 39 cubic millimeters of argon and 0.77 cubic millimeters of xenon. This gives a Xe/A ratio of 0.02 compared to 0.00001 in the atmosphere. The age of this ore determined by the lead-uranium ratio was 1.85×10^9 years. This work indicated that appreciable quantities of xenon, possibly arising from fission, could be expected in uranium ores. Late in 1949 the rare gases were extracted in this laboratory from a sample of Great Bear Lake pitchblende in sufficient quantities to determine the mass yield curve for spontaneous fission by mass spectrometer measurements. Preliminary results of this work including the detection of fission product krypton have already been published[16].

EXPERIMENTAL

Gas Extraction Apparatus

The apparatus used in this laboratory for the extraction and purification of xenon and krypton from irradiated uranium metal has been described elsewhere[17]. The same apparatus, with minor modifications, was used for the pitchblende samples. The anhydrous magnesium perchlorate in the first U tube of the drying train was replaced with Ascarite to absorb the carbon dioxide produced from carbonates in the pitchblende. A calcium furnace was installed immediately following the drying train and separated from it by a stopcock. This furnace was used for initial purification of the gas which contained large amounts of oxygen and nitrogen from air occluded in the pitchblende. The remainder of the apparatus and the final purification and volume measurement was identical to that described previously[17]. The pitchblende was dissolved in concentrated sulfuric acid for 1½ hours. Preliminary experiments showed that negligible gas was released after the first hour.

Mass Spectrometry

All samples were analysed on a 180° direction focussing mass spectrometer. The sample line of this instrument was constructed entirely of capillary tubing to reduce the volume for handling small samples. The D. C. Amplifier was replaced with an Applied Physics Corporation Vibrating Reed Electrometer which, with a grid resistor of 5×10^{10} ohms, gave a satisfactory zero line with a sensitivity four times that obtainable with a conventional feedback D. C. Amplifier. To further increase the sensitivity the trap current (electron beam or ionizing current) was increased from the normal 30 microamperes to 450 microamperes. All samples were analysed with a repeller voltage of +14 to accelerate the ions towards the initial slit and with the energy of the ionizing electrons at 60 electron volts.

Calibration of the Mass Spectrometer for Xe/Kr Determinations

The combined volume of xenon and krypton extracted from the pitchblende samples was approximately 10^{-4} cubic centimeters at N.T.P. This is too small a volume to permit the xenon and krypton to be separated as was done in the case of the neutron fission work[17]. Therefore, a determination of the Xe/Kr ratio in spontaneous fission by volume measurements is not possible. Before the Xe/Kr ratio could be determined from the mass spectrometer results it was necessary to calibrate the mass spectrometer with mixtures of xenon and krypton of known composition. Standard mixtures of xenon and krypton, with Kr/Xe ratios covering the range from 0.5 to 6.0 were prepared using the gas pipetting system on the gas extraction apparatus. The volumes were checked by measurement in the calibrated McLeod gauge before the two gases were mixed. The ratios are accurate to ± 1%. The total volume of a standard mixture was kept between 5 and 10 cubic millimeters to permit analysis under approximately the same conditions as the samples extracted from pitchblende.

Experiments were conducted to determine the extent of Xe-Kr fractionation which occurred in removing the mixture from the sample tube charcoal. It was found that little or no fractionation occurred if the charcoal were heated to 200°C. or higher. In the actual calibration the standard samples were removed from the charcoal traps at 250°C.

It was found that the measured Kr/Xe ratio changed slowly with time for each sample. This change was undoubtedly due to fractionation at the leak since the small size of the samples and the low pressures permit considerable mixing between the gas in the sample line reservoir and the gas at the leak. Thus any fractionation at the leak would soon be reflected in a change in the composition of the gas in the sample line reservoir. To correct for this fractionation all results were plotted against time and extrapolated to zero time in the sample line. Distance measured along the recorder chart from the time of admission of the sample into the sample line was used as a time scale. The chart speed of the recorder is approximately 10 centimeters per minute. The results of a typical extrapolation are shown in Figure I. The Kr/Xe calibration results are given in Table II and are shown graphically in Figure II. The straight line through the origin in this figure has been fitted by the method of least squares and corresponds to the true Kr/Xe ratio equal to the measured ratio multiplied by 1.605. The largest deviation from the straight line is 3% for sample number 4 hence it is reasonable to assume that the calibration is accurate to ± 3% over the range covered by the calibration samples.

Age Determination

The pitchblende samples were crushed in an iron mortar until fine enough to pass through a 40 mesh screen. Samples of about 100 grams were removed for age determinations and the remainder was set aside for the extraction of the rare gases. The age of the pitchblende was determined by two methods; (i) from the lead-uranium ratio and (ii) from the Pb^{207}/Pb^{206} ratio[18]. The numbers of atoms of radiogenic lead in a

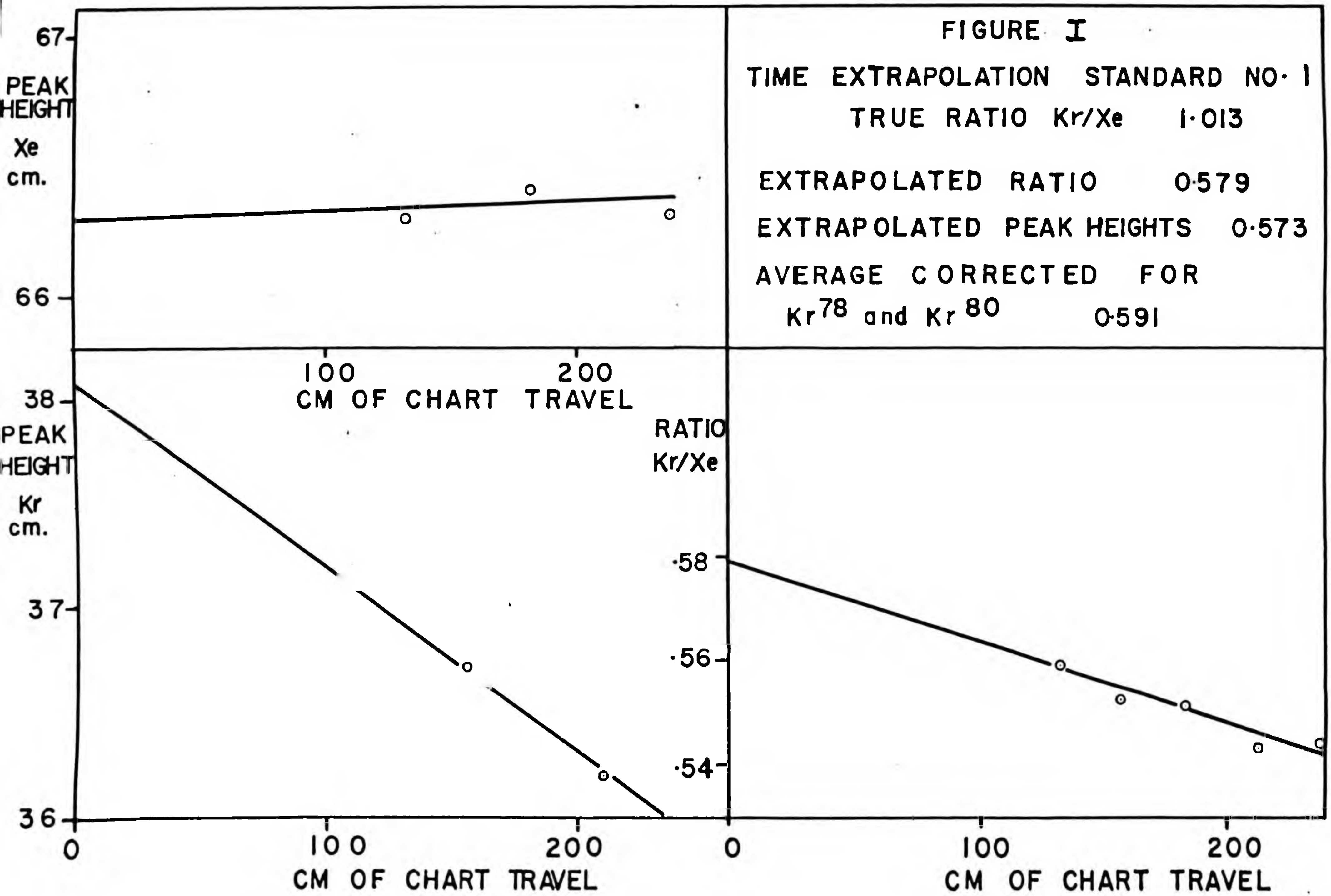


FIGURE I
TIME EXTRAPOLATION STANDARD NO· 1
TRUE RATIO Kr/Xe 1·013
EXTRAPOLATED RATIO 0·579
EXTRAPOLATED PEAK HEIGHTS 0·573
AVERAGE CORRECTED FOR
Kr 78 and Kr 80 0·591
PEAK HEIGHT Xe cm.
67
66
100
200
CM OF CHART TRAVEL
PEAK HEIGHT Kr cm.
38
37
36
0
100
200
CM OF CHART TRAVEL
RATIO Kr/Xe
·58
·56
·54
0
100
200
CM OF CHART TRAVEL

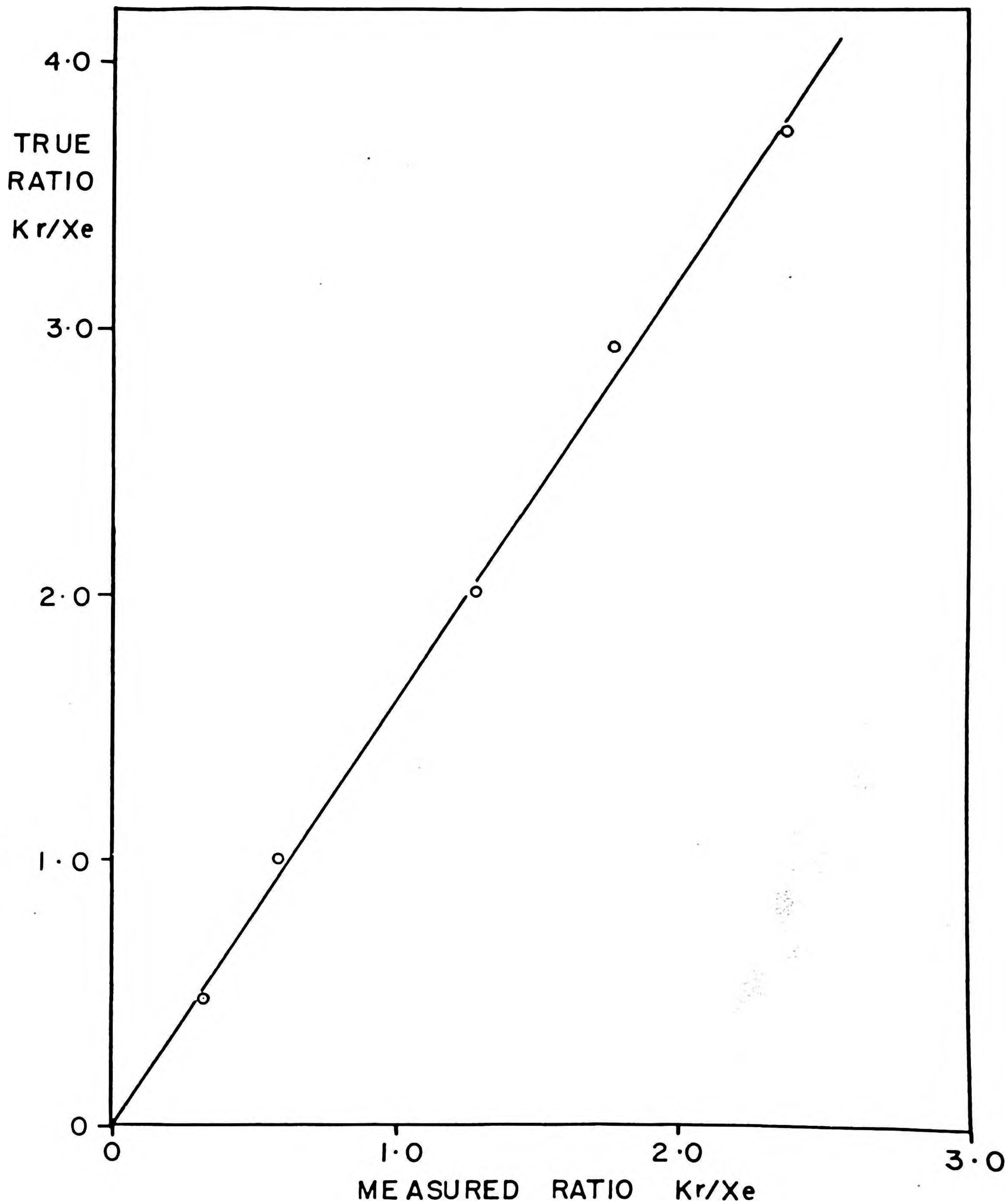
TABLE II

Kr/Xe CALIBRATION

SAMPLE NUMBER	TRUE RATIO Kr/Xe	MEASURED RATIO Kr/Xe
1	1.013	0.591
2	2.012	1.270
3	0.4821	0.317
4	2.934	1.775
5	3.755	2.367

FIGURE II

Kr/Xe CALIBRATION CURVE
180° MASS SPECTROMETER



pitchblende sample containing no thorium are given by the following equations where t is the age of the sample.

$$N(Pb^{206}) = N(U^{238})\left(\exp\left[\lambda(U^{238})t\right] - 1\right) \quad ....(1)$$

$$N(Pb^{207}) = N(U^{235})\left(\exp\left[\lambda(U^{235})t\right] - 1\right) \quad ....(2)$$

Equation (1) gives the age of the sample directly in terms of the lead-uranium ratio. The accuracy of this determination can be greatly improved by using the results of mass spectrometric analysis of the lead to correct for the presence of normal lead in the pitchblende.

Dividing equation (2) by (1) gives the age in terms of the Pb^{207}/Pb^{206} ratio.

$$\frac{Pb^{207}}{Pb^{206}} = \frac{N(U^{235})}{N(U^{238})} \; \frac{\exp\left[\lambda(U^{235})t\right] - 1}{\exp\left[\lambda(U^{238})t\right] - 1} \quad ....(3)$$

At the time of Nier's original work the value of $\lambda(U^{235})$ was not known with any degree of precision. Because of this, equation (3) was written in the form:

$$\frac{Pb^{207}}{Pb^{206}} = \frac{1}{139.0} \; \frac{\exp\left[139.0 \; R\,\lambda(U^{238})t\right] - 1}{\exp\left[\lambda(U^{239})t\right] - 1} \quad .... (4)$$

where $R = N(U^{235})\,\lambda(U^{235}) \;/\; N(U^{238})\,\lambda(U^{238})$

and $N(U^{238}) \;/\; N(U^{235}) = 139.0$ (from mass spectrometer measurements (19).)

The value of R was then chosen to give the best experimental agreement between the lead-uranium age and the lead isotope ratio age for fourteen pitchblende samples. This led to a value for R of 0.045. Recently the value of $\lambda(U^{235})$ has been measured by Fleming, Ghiorso and Cunningham[20] with considerable accuracy and is $9.80 \pm 0.15\times10^{-10}\ yr^{-1}$. Using this value and $\lambda(U^{235}) = 1.54x10^{-10}$ yr^{-1} along with $N(U^{238})/N(U^{235}) = 139.0$ the experimental value of E is 0.0458 in excellent agreement with the value chosen by Nier.

The age determined by the lead isotope method is less likely to be affected by geological alterations which may result in the loss of some uranium or some lead and for this reason is probably the more accurate of the two values and is the value used in this work. Good agreement between the ages determined by the two methods indicates that there has been little alteration of the deposit and that therefore it is possible that most of the rare gases formed have been retained.

The ages of three pitchblende samples have been determined and are given in Table III. The chemical analysis for lead and uranium was performed by Eldorado Mining and Refining. The lead isotope ratios were determined in this laboratory on a double focussing mass spectrometer by Mr. W. H. Walker. Duplicate samples were sent to the mass spectrometer group at the University of Toronto for analysis. The agreement between the two sets of results is quite good considering the difficulty in correcting for the contribution of normal lead in the samples. The results obtained by Mr. Walker in this laboratory have been used throughout this work. It appears that the Lake Athabaska sample has undergone considerable alteration because of the large difference between the lead-uranium and lead isotope ratio age. This sample also has a low uranium content and for this reason no attempt has been made at present to extract the rare gases.

TABLE III

PITCHBLENDE AGES

SAMPLE	AGE (YEARSx10^6)		
	LEAD-URANIUM	LEAD ISOTOPE	
		McMASTER	TORONTO
Great Bear Lake	1202	1386	1390
Katanga Belgian Congo	699	635	625
Lake Athabaska	1372	1720	1690

Rare Gas Extraction and Analysis.

Samples of pitchblende, from 150 to 200 grams, were heated in vacuo to above 200°C. for from 1 to 2 hours to remove most of the adsorbed gases. The 500 ml of concentrated sulfuric acid used for the dissolution of the pitchblende was first heated in vacuo and then flushed 15 times with hydrogen in an effort to remove all gases. The sulfuric acid was then transferred to the pitchblende in the dissolution flask and the reaction was allowed to proceed for 1½ to 2 hours at about 100°C. The gases formed were condensed in a charcoal trap at liquid air temperature after passing through the drying train. After passing through the charcoal trap the non-condensable gases, hydrogen and helium, were pumped off at such a rate as to maintain a pressure of 1 to 3 cm. Hg in the dissolution vessel.

The amount of gas condensed in the charcoal trap was sufficient to produce about 5 cm. Hg pressure in the preliminary calcium furnace which has a volume of approximately 150 ml. After the preliminary calcium furnace the pressure dropped to about 1 mm. Hg. The main contaminations probably are nitrogen and oxygen. The gas was then transferred to the second calcium furnace for final purification after which the volume of the sample was approximately 30 cubic millimeters at N.T.P. as measured by the calibrated McLeod guage. The gas was then condensed on to the sample tube charcoal and removed from the line for mass spectrometer analysis.

Preliminary mass spectrometer analysis showed the samples to contain approximately 99.89% argon, 0.038% krypton, and 0.075% xenon. This is a much higher ratio of argon to xenon than reported by Khlopin and his associates[15] and indicates that there is some source of rare gas contamination in the present work. Experiments were then conducted to determine the possible sources of this rare gas contamination.

The first possibility considered was that the excess argon might have been formed by the decay of K^{40} in the pitchblende. If this were the case the abundance of the argon isotopes extracted from the pitchblende would probably be quite different than in the atmosphere. Mass spectrometer analysis of this argon showed that the isotopic constitution was not significantly different from that of normal argon. K^{40} was definitely ruled out as a source of argon in the pitchblende when it was found that the Belgian Congo pitchblende yielded nearly the same amount of argon as the Great Bear Lake ore. The argon from the Belgian Congo sample was also of normal isotopic composition.

The gases dissolved in sulfuric acid were then studied by Mr. R. K. Wanless with the aid of a 90° mass spectrometer. It was found that relatively large amounts of argon were present in sulfuric acid and could be released by heating. However heating to the boiling point would not remove all the argon since almost equal quantities could be released by subsequent reheating. It is important that all of the argon be removed from the acid used to dissolve the pitchblende since the presence of argon indicates that normal krypton and xenon are also present although in much smaller quantities. It was thought that a combination of heating and flushing with hydrogen would remove the majority of any gases dissolved in the acid. This procedure was therefore adopted for all subsequent rare gas extractions but no decrease in the amount of argon or normal krypton and xenon was observed.

The hydrogen used was commercial tank hydrogen supplied by Canadian Liquid Air Company and was passed over charcoal at liquid nitrogen temperature to remove any impurities present. Quite recently, however, it was found that even after this treatment the hydrogen contained approximately 0.003% of rare gases composed almost entirely of argon with very small traces of krypton and xenon. It is known that xenon and krypton are completely removed from hydrogen by this treatment when it is carried out at a reduced pressure of the order of 5 cm. Hg or less. Under these conditions the argon is removed to the extent of about 99%. It is necessary to fill the hydrogen reservoir on the extraction line to approximately atmospheric pressure to provide for efficient transfer of the acid to the dissolving flask against the pressure produced by the reaction with the pitchblende. Apparently at this pressure the charcoal is no longer capable of removing the rare gases to any great extent.

RESULTS

The presence of small peaks at masses 128 and 130 in the xenon spectrograms disclosed the presence of normal xenon in the samples as well as fission product xenon. Similarly the presence of a peak at mass 82 in the krypton spectrograms indicated some normal krypton. All results were corrected for the presence of normal krypton and xenon using the isotope abundance data reported by Lounsbury, Epstein, and Thode[21]. This correction can be made with considerable accuracy for the xenon isotopes since the relative amount of normal contamination is small but in the case of krypton the normal correction is larger than the final yield values and considerable error is introduced.

Xenon Fission Yields

In this work the yield of the 136 mass chain has been arbitrarily chosen to be 6.00% and all other yields have been calculated relative to this value. The results of a typical double scan spectrogram of xenon from the Belgian Congo pitchblende are given in Table IV to show the magnitude and effect of the normal xenon correction. It can be seen from these results that the accuracy of the normal xenon correction has a large effect on the final yield value particularly for mass 129 where the normal contamination is much larger than the fission product contribution. Accurate correction for normal xenon is not possible at the present time since the small size of the samples limits the peak height and hence the accuracy with which the 130 peak can be measured. The uncertainty in the height of the 130 peak in the above case is roughly 30%. The effect of this is to cause wide fluctuations in the 129 yield value in

TABLE IV

TYPICAL XENON SPECTROGRAM RESULTS

MASS	PEAK HEIGHT (cm.) UP SCAN	DOWN SCAN	TOTAL	CORRECTION (cm.)	FISSION PRODUCT (cm.)	% YIELD UNCOR.	CORR.
129	2.68	2.37	5.05	4.19	0.86	1.01	0.18
130	0.37	0.27	0.64	0.64	0	0	0
131	4.63	4.71	9.34	3.37	5.97	1.86	1.25
132	10.98	10.50	21.48	4.28	17.20	4.28	3.60
134	14.39	14.16	28.55	1.66	26.89	5.69	5.62
136	15.04	15.05	30.09	1.41	28.68	6.00	6.00

TABLE V

GREAT BEAR LAKE XENON FISSION YIELDS

RUN NUMBER	NUMBER OF DETERMINATIONS	% IN FISSION 129	131	132	134	136 #
1	6	0.0764	0.721	3.43	5.08	6.00
2	4	0.117	0.772	3.47	5.10	6.00
3	4	0.0519	0.712	3.42	5.09	6.00
4	7	0.089	0.754	3.48	5.12	6.00
5	4	0.063	0.734	3.45	5.10	6.00
6	2	0.0468	0.683	3.31	5.16	6.00
7	3	0.114	0.75	3.43	5.10	6.00

#assumed value

The weighted average of the 30 determinations is:

129	0.082 ± .036
131	0.737 ± .034
132	3.44 ± .02
134	5.10 ± .03
136	6.00

TABLE VI

BELGIAN CONGO PITCHBLENDE XENON FISSION YIELDS

RUN NUMBER	NUMBER OF DETERMINATIONS	% IN FISSION 129	131	132	134	136 #
1	12	0.228	1.187	3.64	5.56	6.00
2	6	0.186	1.15	3.59	5.57	6.00
3	6	0.176	1.16	3.60	5.57	6.00

assumed value

The weighted average of the 24 determinations is:

129	0.205±.039
131	1.17±.04
132	3.62±.05
134	5.57±.03
136	6.00

successive scans of the same sample.

The xenon yields determined from seven different runs on Great Bear Lake pitchblende are given in Table V and the results of three different runs on Belgian Congo pitchblende in Table VI. All yields have been corrected for normal xenon. It can be seen from these tables that the results of separate extractions from the same pitchblende are in good agreement with each other. The deviations given in the tables are the "standard deviations". None of the separate results differ from the averages given by as much as three times the standard deviations.

Krypton Fission Yields

The determination of the krypton fission yields is more difficult than in the case of xenon for two reasons. In the first place the actual yields are much lower which makes it more difficult to obtain accurate measurements. In the second place the amount of normal krypton present is much greater than the amount of normal xenon which increases the errors introduced in correcting for the normal contamination. All krypton results were corrected for normal krypton in the same manner as in the case of xenon. The results of four samples from the Great Bear Lake pitchblende are given in Table VII and the results of three samples from the Belgian Congo pitchblende in Table VIII. These results are given in terms of percent of total fission product krypton since the actual fission yields depend on the Kr/Xe ratio which was measured in a separate determination.

It can be seen that the reproducibility and precision of the krypton results are not as good as in the case of xenon. The measured ratios of fission product xenon to fission product krypton are:

TABLE VII

FISSION PRODUCT KRYPTON ABUNDANCES GREAT BEAR LAKE PITCHBLENDE

RUN NUMBER	NUMBER OF DETERMINATIONS	ATOM PERCENT ABUNDANCE 83	84	86
1	1	2.94	26.5	70.6
2	1	4.82	18.1	77.1
3	9	5.36	20.3	74.4
4	4	2.97	21.9	74.8

The weighted average of the 15 determinations is:

83	4.52 ± 1.51
84	21.0 ± 4.0
86	74.0 ± 3.3

TABLE VIII

FISSION PRODUCT KRYPTON ABUNDANCES BELGIAN CONGO PITCHBLENDE

RUN NUMBER	NUMBER OF DETERMINATIONS	ATOM PERCENT ABUNDANCE 83	84	86
1	5	14.7	16.5	67.9
2	6	11.7	18.7	69.6
3	5	10.7	26.8	62.5

The weighted average of the 16 determinations is:

83	12.3 ± 2.6
84	20.5 ± 5.7
86	66.8 ± 5.6

Great Bear Lake	10.3
Belgian Congo	7.4

The krypton fission yields calculated using these values in conjunction with Tables VII and VIII are given in Table IX.

TABLE IX

MASS	% IN FISSION	
	GREAT BEAR LAKE	BELGIAN CONGO
86	1.10±.05	1.50±.12
84	0.31±.06	0.46±.13
86	0.067±.022	0.28±.06

DISCUSSION

Xenon Fission Yields

It is known that, for neutron fission of U^{235} and U^{238}, the depth of the trough between the humps of the mass yield curve decreases with increasing neutron energy. For this reason it would be expected that, for spontaneous fission where no energy is added to the nucleus before fission takes place, this trough would be much deeper and that the slope of the sides of the humps of the mass yield curve would accordingly be much steeper. That this is the case can be seen from Figure III where the xenon yields from Great Bear Lake and Belgian Congo pitchblendes are plotted along with the U^{235} +n mass yield curve. The spontaneous yield curves may be shifted up or down slightly depending on the value assigned to Xe^{136} but this will not effect the shape of the curves. The U^{238} +n mass yield curve is not shown because no yield measurements have yet been reported in the mass range 129 to 136. However from the shape of the U^{238} curve in other regions it is expected to be a parallel curve to the U^{235} curve in this region but with all yields slightly lower. The linear plot was chosen rather than the usual logarithmic plot because the uncertainty in the measurement of the 129 yield does not permit an accurate logarithmic representation.

The yields of the 132 mass chain fall considerably above the smooth curve drawn through the remainder of the points for both samples. For the Great Bear Lake sample the 132 yield is approximately 95% above the smooth curve while the Belgian Congo value is approximately 45% high. Previous work at this laboratory[(2)] has shown that for neutron fission

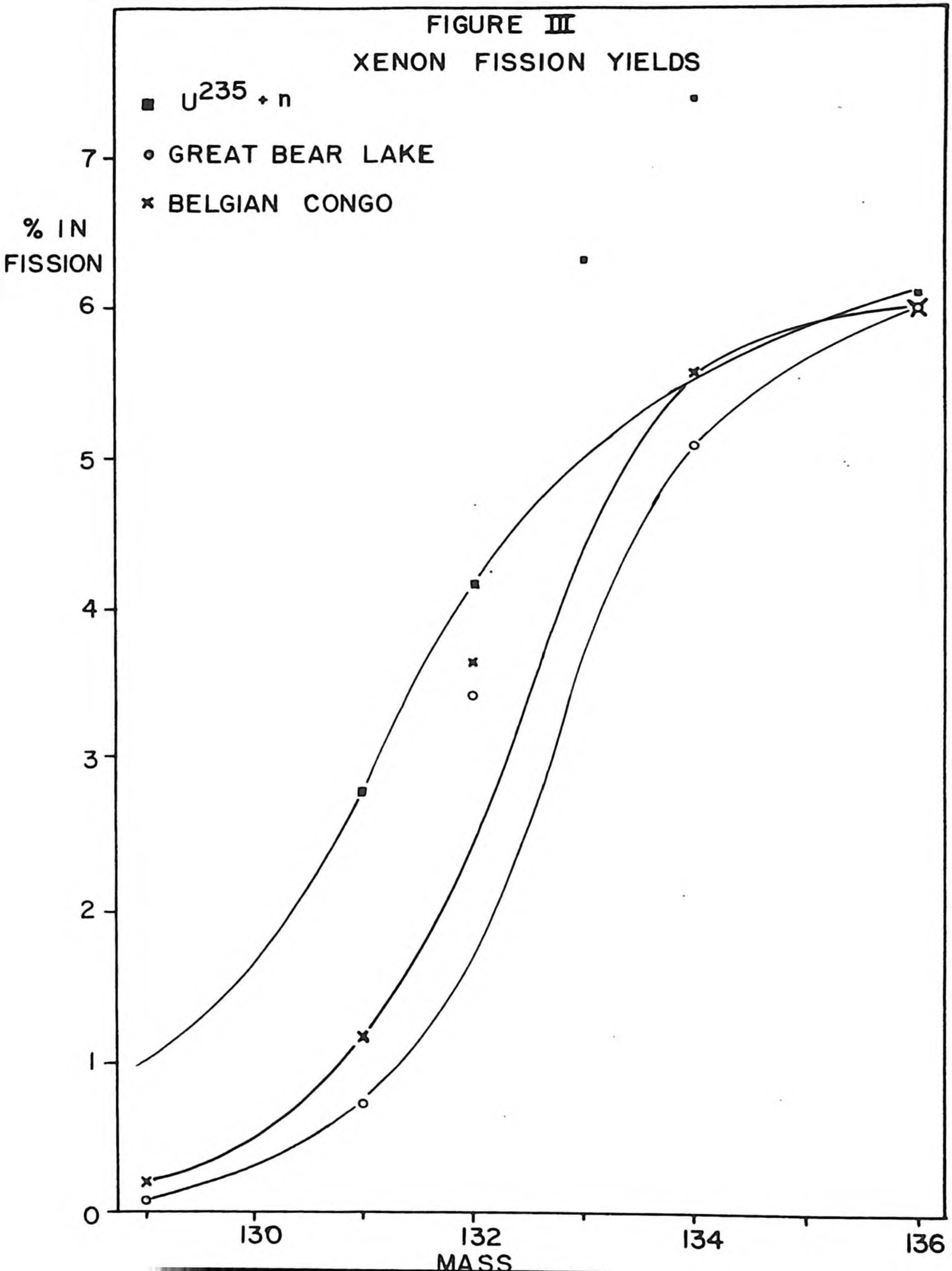


FIGURE III
XENON FISSION YIELDS
U^{235} + n
GREAT BEAR LAKE
BELGIAN CONGO
% IN FISSION
0
1
2
3
4
5
6
7
130
132
134
136
MASS

of U^{235} the 133 and 134 yields are 26% and 35% above the smooth curve respectively. These points are also shown in Figure III. This fine structure in the mass yield curve is undoubtedly related to the stable 82 neutron shell and has been attributed by Glendenin[23] to the emission of a neutron by a nucleus with one neutron in excess of the closed shell when this nucleus is formed as a primary fission product. The decay chains in the neighbourhood of the 82 neutron shell together with the proposed neutron emissions are shown in Table X. It is interesting to note that Xe^{137} which is one of the proposed neutron emitters in this table is one of the known delayed neutron emitters in fission. If the Glendenin mechanism is the correct explanation of the fine structure it is evident that, for neutron fission of U^{235}, Sb^{134} and Te^{135} are formed in a high primary yield. For fission of U^{238}, spontaneous or neutron induced, the high primary yields in each mass chain will be shifted to the left in Table X towards higher numbers of neutrons because of the higher mass and higher neutron to proton ratio in the fissioning nucleus. The primary yield of Te^{135} will be decreased while the primary yield of Sn^{133} will be increased. This will result in a shifting of the fine structure towards the lower masses. It is probable that the primary yield of Sb^{134} will still be quite high so that the fine structure for U^{238} fission would be expected at masses 132 and 133. That the 132 yield is high is obvious from the pitchblende results but unfortunately it is impossible to determine the 133 mass chain yield for these samples because of the short half life of Xe^{133}. Since Cs^{133} is the only stable isotope of cesium it is not possible to determine the 133 mass chain yield at its stable end product because it would be impossible to

TABLE X

MASS	FISSION PRODUCT DECAY CHAINS						
	ELEMENT						
131	Sn	Sb	Te	I	Xe Stable		
132	Sn	Sb	Te	I	Xe Stable		
133	Sn	Sb	Te	I	Xe	Cs Stable	
134		Sb	Te	I	Xe Stable		
135		Sb	Te	I	Xe	Cs	Ba Stable
136		Sb	Te	I	Xe Stable		
137			Te	I	Xe	Cs	Ba Stable

tell what percentage of the total cesium present in the pitchblende was normal cesium and what percentage fission product.

Evidence supporting the Glendenin theory of fine structure has been obtained in the preliminary results for uranium irradiated with fast neutrons in the Los Alamos pile in which there has been a combination of U^{235} and U^{238} fission. In this sample both the 134 and 132 yields are above the smooth curve. Because of this it is logical to assume that a high yield of the 132 mass chain is a characteristic of U^{238} fission. Combined with the absence of appreciable fine structure at mass 134 in the pitchblende samples this indicates that the only uranium isotope which contributes appreciably to spontaneous fission in pitchblende is U^{238}. This is in agreement with the half life measurements reported by Segre(9).

It can be seen from Figure III that the xenon yields from the Belgian Congo pitchblende lie closer to the U^{235} yield curve than those from Great Bear Lake pitchblende. Before the half life measurements of Segre were available it was thought that this difference might be explained by assuming a combination of U^{235} and U^{238} spontaneous fission. Since the theoretical work of Flugge(12) predicted the half life for fission of U^{235} to be one thousand times shorter than that of U^{238} the small percentage of U^{235} in natural uranium could account for a large fraction of the total fissions. As the amount of U^{235} in uranium today is independent of the age of the ore it follows that at the times of formation the Great Bear Lake sample would have contained a much higher percentage of U^{235} than the Belgian Congo ore. Consequently the Great Bear Lake ore today would contain more fission product gases from U^{235}

is the rate of formation is equal to the decay rate. This may be represented mathematically as follows:

$$\lambda(Pu^{239})N(Pu^{239}) = F\sigma N(U^{238}) \quad \text{..........} (1)$$

where F is the neutron flux
and σ is the capture cross section of U^{238}.

If the spontaneous fission neutron energy spectrum and the capture cross section versus energy relation for U^{238} were known it would be possible to calculate the neutron flux in the pitchblende. The number of neutron fissions of the uranium isotopes could then be calculated as follows:

$$\text{Fission rate } U^{235} = F\,\sigma_f(U^{235})N(U^{235}) \quad \text{......}(2)$$

$$\text{Fission rate } U^{238} = F\,\sigma_f(U^{235})N(U^{235}) \quad \text{......}(3)$$

A rough approximation of the magnitude of this neutron fission has been made using equation (2) and the values given by the Chalk River Group (10) for the thermal neutron cross sections. The results of this calculation are:

Great Bear Lake 7×10^{17} fissions per Kg U.

Belgian Congo 6×10^{17} fissions per Kg U.

These values represent upper limits since the large thermal neutron fission cross section was used in the calculations. These numbers of neutron fissions are of the same order of magnitude as the numbers of spontaneous fissions expected which are

Great Bear Lake 3.3×10^{17} fissions per KgU.

Belgian Congo 1.8×10^{17} fissions per Kg U.

While these neutron fission estimates give only an order of magnitude, the values relative to each other should be reasonably accurate. They indicate that the contribution of neutron fission to the total fission product gas available will be nearly twice as great in the Belgian Congo pitchblende as in the Great Bear Lake sample. The effect of this would be to make the Belgian Congo yields fall closer to the U^{235} +n curve as is in fact observed. The relative separation of the 132 yield from the smooth curve through the remainder of the points should be decreased by this effect and some indication of fine structure at mass 134 should be apparent. The fine structure at mass 132 is definitely less prominent in the Belgian Congo sample and there is some indication that the 134 yield is high since the separation between the two yield curves is greatest at this point.

The number of neutron induced fissions may be greatly increased in a sample of ore by the presence of some impurity which could act as a moderator to slow the neutrons down to thermal energies where the U^{235} fission cross section is very large. Experimental evidence for the occurrence of such a slowing down process has been given by J. B. Orr[25]. It is probable that the decrease in neutron energy would cause a much larger increase in the fission cross section of U^{235} than in the capture cross section of U^{238} and hence the occurence of this effect would not be evidenced by an extraordinary high Pu/U ratio. It is suggested that such a slowing down of neutrons could have taken place in the Belgian Congo pitchblende since the difference between the xenon yield curves for the two samples is too large to be accounted for by a difference of a factor of two in the contribution of neutron fission to the total fission product gas present in the ores.

Further information is needed to explain fully the xenon results obtained to date. Samples of pitchblende, differing widely in age and chemical composition, are now being investigated to determine the effect of age and composition on the shape of the mass yield curve.

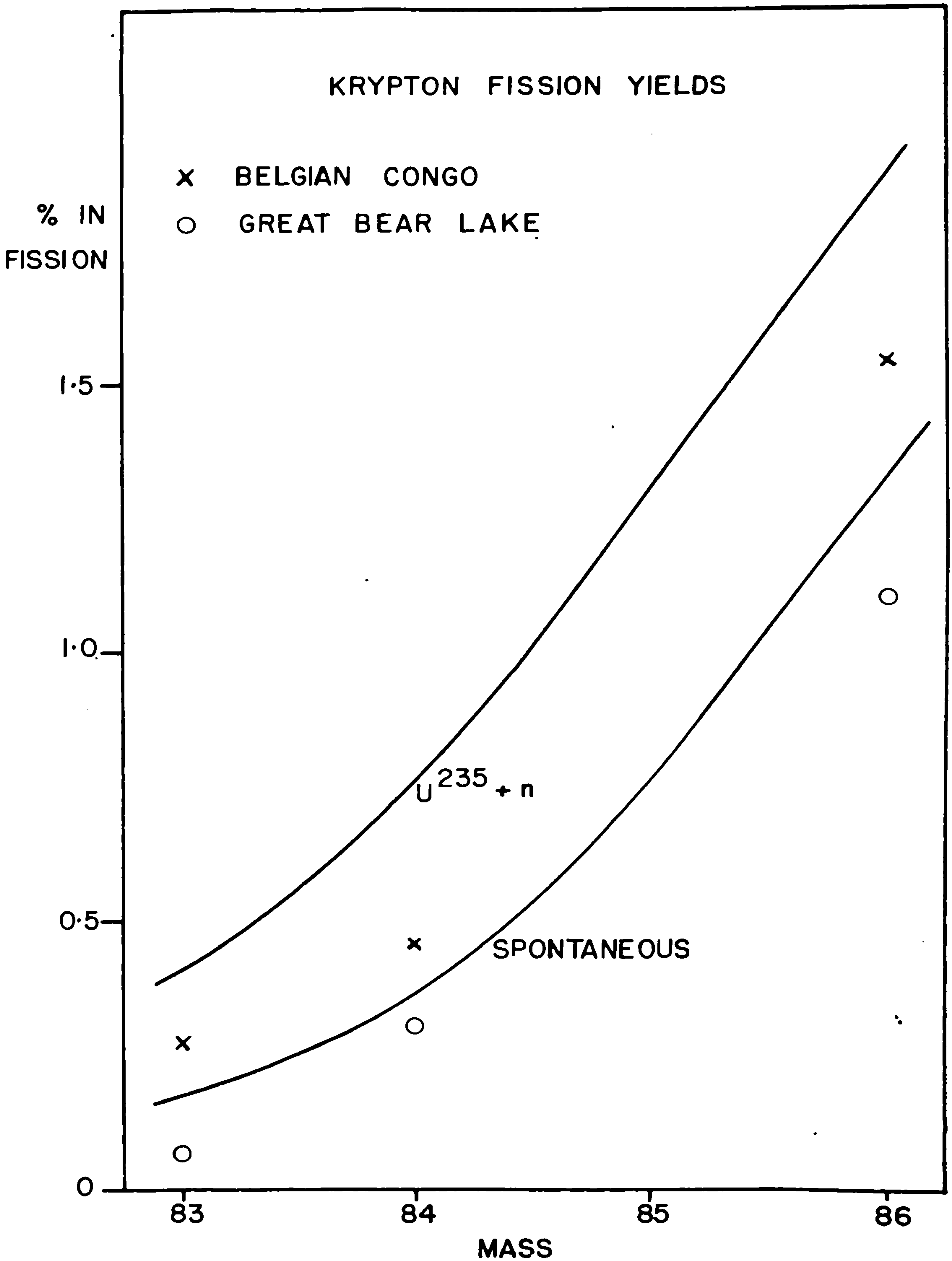
Krypton Fission Yields

It has been found that, for neutron fission of U^{238}, the mass yield curve in the krypton region has been shifted towards the higher masses by approximately one mass unit relative to the U^{235} +n curve. That the same is true for the spontaneous fission of U^{238} can be seen from Figure IV where the krypton fission yields for the pitchblende samples are plotted along with the U^{235} +n curve. Because of the large deviations in the krypton results and the possible error introduced into the Xe/Kr ratio measurement by the large amount of normal krypton contamination separate yield curves have not been drawn for the Belgian Congo and Great Bear Lake samples.

Although the krypton fission yields are less reliable than the xenon values for reasons mentioned earlier, the results of a large number of determinations indicate that the slope of the mass yield curve for spontaneous fission is not appreciably steeper than that of the U^{235} +n curve in the mass range 82 to 86. This is in agreement with the observation that, in neutron fission, increasing neutron energy has a large effect on the portion of the mass yield curve between the two humps but less effect on the outer portions of the curve.

If the difference between the xenon yields from the two samples is due to a larger proportion of neutron fission of U^{235} in the Belgian Congo pitchblende it would be expected that the krypton yields from the

FIGURE IV



KRYPTON FISSION YIELDS
× BELGIAN CONGO
○ GREAT BEAR LAKE
% IN FISSION
1·5
1·0
0·5
0
U^{235} + n
SPONTANEOUS
83
84
85
86
MASS

Belgian Congo pitchblende would lie closer to the U^{235} +n curve than those from the Great Bear Lake ore. There is some indication that this is indeed the case but more accurate krypton yield data must be obtained before a definite conlusion can be reached on this point.

Overall Shape of the Spontaneous Fission Mass Yield Curve

The xenon and krypton yield values determined are sufficient to give a fairly good idea of the overall shape of the mass yield curve for the spontaneous fission of U^{238}. If it is assumed that this curve is symmetrical about mass 118, that is two neutrons per fission, the xenon and krypton results give the equivalent of eight points on each hump of the curve. Figure V shows the mass yield curve drawn on this assumption and also the U^{235} +n curve for comparison. In drawing this curve the Great Bear Lake xenon results were taken as being the more representative of the true spontaneous fission yields in this range. The entire curve should be shifted up or down slightly to achieve a total of 100% yield under each half of the curve but more data at different mass values is required to do this accurately.

Increased Accuracy of the Yield Determinations

The small percentage of rare gases present in the hydrogen is sufficient to produce approximately half of the gas obtained from the pitchblende extractions. This has been shown by blank runs without acid or pitchblende using the same amount of hydrogen used in a normal extraction. Two runs have just been completed, one with Great Bear Lake and one with Belgian Congo pitchblende, in which the dissolution flask was not flushed with hydrogen after the end of the dissolution period. Both

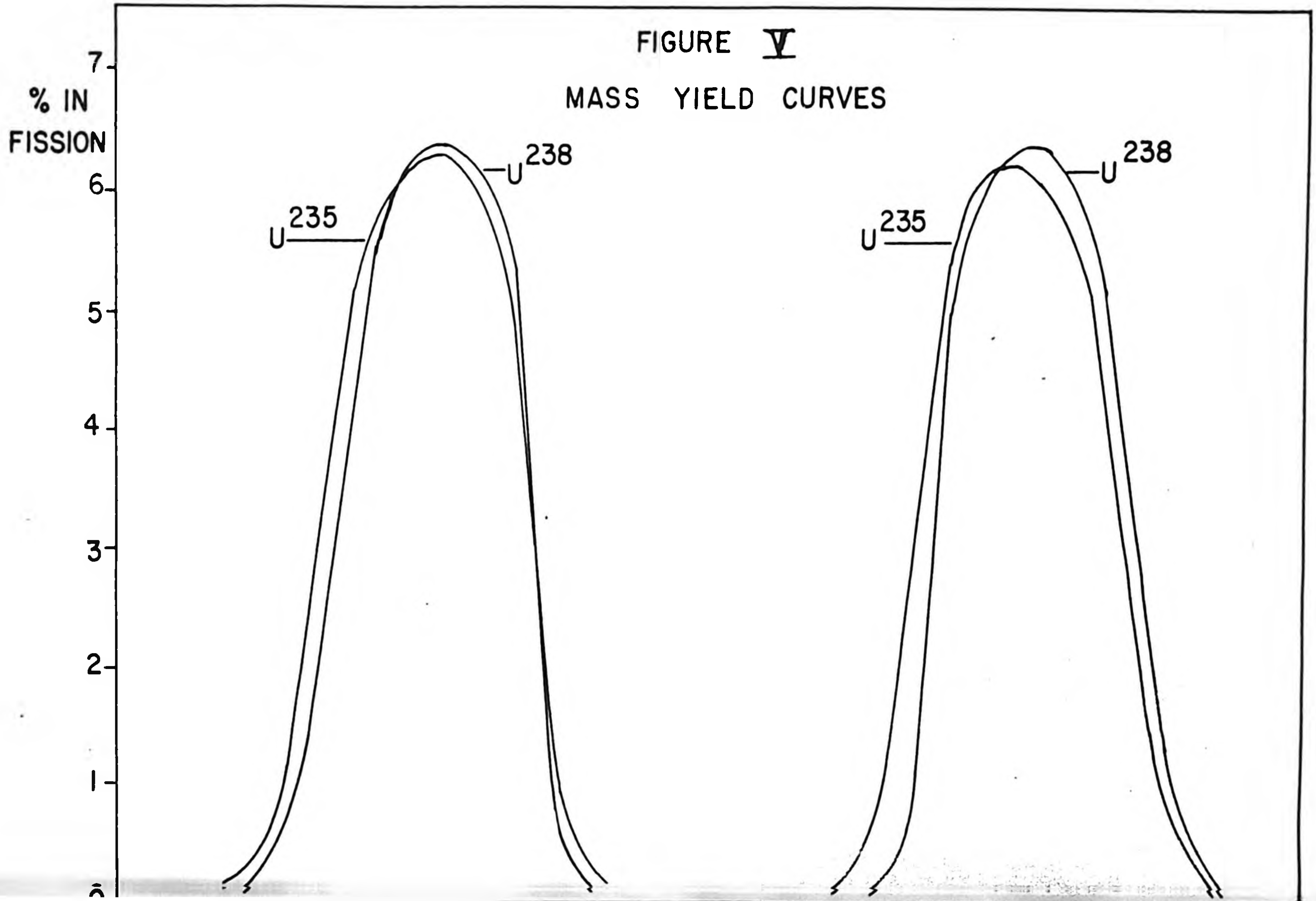


FIGURE V

MASS YIELD CURVES

of these samples were smaller in total volume and contained considerably less normal xenon and krypton indicating that the hydrogen is a major source of normal contamination. Complete purification of the hydrogen, possibly accompanied by refluxing the acid in vacuo, should result in a large reduction in the amount of normal gases present and a corresponding increase in the accuracy of the fission yield measurements. Some normal xenon and krypton is to be expected in the pitchblende itself but this amount should be relatively small. The only gases besides hydrogen which are suitable for this use, that is which will not condense on charcoal at liquid air temperature, are helium and neon which are more likely to contain xenon and krypton than hydrogen.

If the overall sensitivity of the mass spectrometer could be increased the accuracy of the fission yield determinations would be greatly increased by the elimination of the errors introduced by the small peak heights. Increased sensitivity can be realized in two ways: (i) by the use of a more efficient ion source and (ii) by a more sensitive ion current measuring system. Both of these possibilities are now being studied.

It is possible that the amounts of xenon and krypton extracted from the pitchblende represent only a small portion of the total fission product gases present since the pitchblende is not completely dissolved by the sulfuric acid. Calculations of the amount of xenon which should be present if the total xenon fission yield is 16% indicate that the procedure used results in the recovery of at least 50% of the xenon available. This value is a lower limit obtained by allowing an error of a factor of two in the mass spectrometer measurement of the ratio of xenon to argon in the samples. Experiments using other acids to dissolve the pitchblende are now being carried out to determine if larger quantities of gas can be released from the pitchblonde. An increase in the size of the samples will result in more accurate yield measurements.

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