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

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SCOPE AND CONTENTS:

The absolute abundances of fission-product xenon and krypton isotopes in six uranium minerals were determined mass spectrometrically using the isotope dilution technique. The fission products were resolved into a U^{238} spontaneous fission component, a U^{235} neutron-induced fission component, and a U^{238} neutron-induced fission component. The presence of U^{238} neutron-induced fission indicated that the neutron energies in uranium minerals were higher than had been suspected. Internal consistency in the analysis was achieved only when the I^{129} yield in U^{235} thermal neutron fission reported by Purkayastha and Martin was lowered by 20%.

The number of U^{238} spontaneous fissions was calculated from the lead age, U^{238} content, and the U^{238} spontaneous fission half life. A comparison of the number of fission products from U^{238} spontaneous fission and the number of spontaneous fissions in each of the six minerals showed that

five of the six minerals had lost large portions of their noble gases. A fractionation of krypton relative to xenon accompanied this loss. The results obtained for the sixth mineral indicated little or no loss of xenon and krypton. Absolute yields for U^{238} spontaneous fission were therefore determined from an analysis of this mineral.

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INTRODUCTION

The Fission Process

The discovery of fission in 1939 by Hahn and Strassmann(1) stimulated many investigations into the nature of the process and its technological implications.

In the fission process, a heavy nucleus splits into two fragments or fission products of approximately equal mass. The fission may be induced by irradiation with particles or photons of suitable energy, or may occur spontaneously. Many decay channels are available to the fissioning nucleus and over 200 fission products have been identified. Most of these products are formed at some distance from the beta-stability line and decay by negatron emission, and in some cases by neutron emission, to stable nuclei. The percent probability per fission of forming a given nuclide, or a given decay chain, is defined as its absolute fission yield. Relative yields, on the other hand, compare two or more fission product yields without reference to the number of fissioning nuclei.

Induced-fission yields can be determined by radiochemical or mass spectrometric techniques. In the radiochemical technique one determines relative yields by counting the relative disintegration rates of fission products and absolute yields by counting not only the absolute disintegration rates, but also the number of fissions which have taken place in an aliquot of fissile material exposed to the same irradiation. In the mass spectrometric method, on the other hand, one determines relative yields by measuring the relative ion currents from two or more stable or long lived isotopes. The isotope dilution technique, together with a monitor to measure the integrated flux, may be used to obtain absolute fission yields. Spontaneous fission yields are obtained in the same way except that the number of fissions may be calculated from the number of fissile nuclei in a sample, the disintegration rate of these nuclei, and the period during which the fission products accumulate.

The mass distribution of the primary fission yields must be symmetric since only binary fission is known to occur. The probability of symmetric fission is in general low, but increases, along with the most asymmetric modes, with increasing irradiation energy in induced fission. The most exhaustively studied fission process is that obtained when the U^{235} nucleus is irradiated with thermal neutrons. The mass-yield curve for this nuclide is shown in Fig.1. The most probable heavy mass occurs at about 140 and the most probable light mass at about 95 for this fission process. It was suggested by Mayer(2) that the high probability of asymmetric fission could be attributed to the extra stability

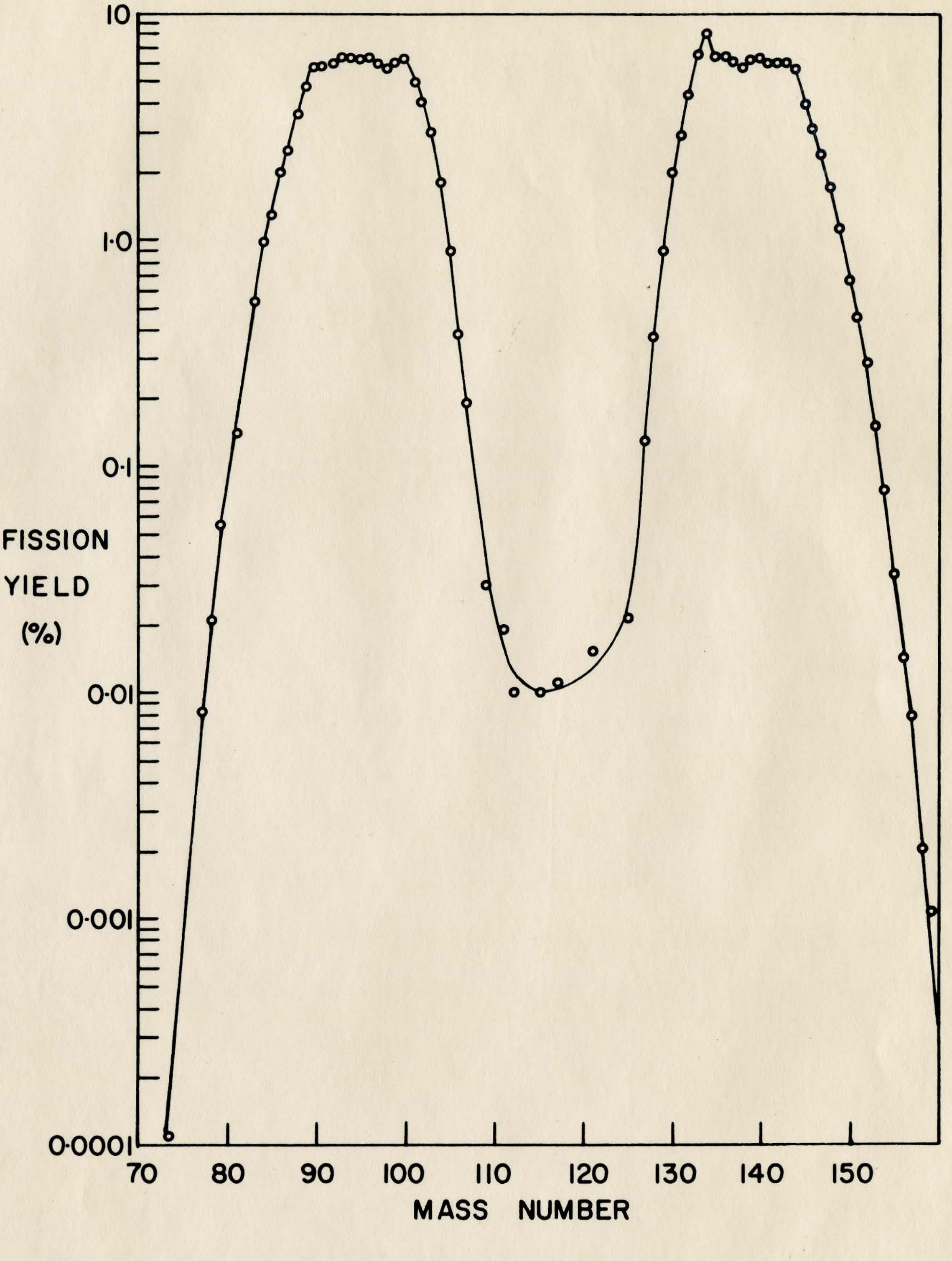

FIG. I MASS-YIELD CURVE FOR U^{235} THERMAL NEUTRON FISSION of the fragment nuclei in the vicinity of the closed shells at 50 and 82 neutrons. Fissions producing fragments of this configuration would be more energetic than those of symmetric fission, and would therefore be more probable.

The measured yield of any nuclide is, with two exceptions, due to its primary yield and the primary yields of nuclides above it in the mass chain. The exceptions are to be found in nuclei with isomeric states, for example Te^{129} and Te^{129m} in Fig.2, and in chains which branch due to neutron emission, for example I^{137} in the 137 mass chain of Fig.2.

Thode and Graham(3) in 1947 reported that the xenon isotopic distribution from U^{235} thermal neutron fission showed a marked fine structure effect at mass 134. Subsequently Glendenin _et al_(4) reported a smaller fine structure effect at the complementary mass 100. The symmetric perturbation in the mass-yield curve was ascribed by Wiles(5)(6) to the preferential formation of fragments containing closed shells of 50 and 82 neutrons. The asymmetric perturbation was ascribed by Glendenin(7) to the emission of neutrons from products near closed shells.

Spontaneous Fission in Uranium Minerals

The spontaneous fission process differs from that of induced fission in that the heavy nucleus, without the addition of energy, is unstable with respect to fission and consequently undergoes fission with a characteristic half life. The control which can be exercised on the induced fission

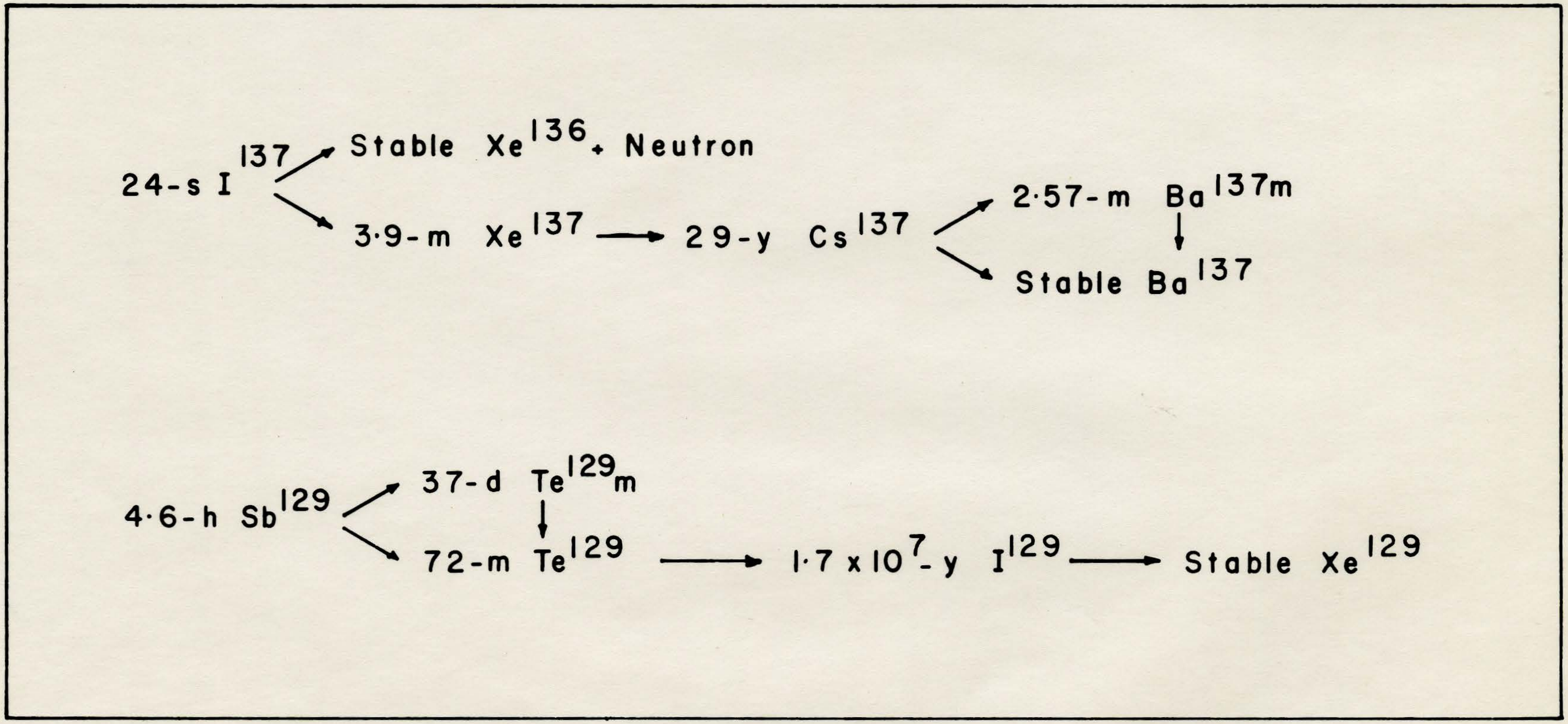

FIG. 2 FISSION PRODUCT CHAINS

rate has made this process of vast importance to technology and has greatly facilitated its laboratory study. Spontaneous fission rates, on the other hand, cannot be controlled, and the process must be studied either in a naturally occurring nuclide of high abundance but low fission rate, or in a synthetic nuclide of low abundance but high fission rate. Consequently, the quantity of fission products which can accumulate in a laboratory experiment is too small for mass spectrometric analysis, and must be measured by the more sensitive, but less accurate, radiochemical techniques.

The spontaneous fission products from naturally occurring fissile nuclei, however, have been accumulating in minerals since their deposition about 10^9 years ago. The U^{238} in old uranium minerals, with a spontaneous fission half life of 8.0×10^{15} years, has undergone about 10^{16} fissions per 100 grams. The more abundant fission products from 10^{16} fissions may be detected and measured on a sensitive mass spectrometer. The relative abundances of the fissile nuclei in uranium minerals, together with their spontaneous fission decay rates(8), have shown that the spontaneous fission products from other nuclei are negligibly small compared to those from U^{238} spontaneous fission. Neutrons, however, may have induced fission in suitable nuclei, and the resulting fission products would then have accumulated with the U^{238} spontaneous fission products.

Stable xenon and krypton fission products that fall on the low mass sides of the high and low mass maxima of the mass-yield curve, respectively, are usually selected for mass spectrometric investigation of U^{238} spontaneous fission in uranium minerals. These isotopes are present in high yield, are relatively free from normal contamination, and are easily purified.

In 1947, Khlopin, Gerling and Barnanovskya(9) reported the presence of excess xenon in pitchblende, and attributed this excess to spontaneous fission products. The first determination of the isotopic distribution of fission product xenon and krypton isotopes in pitchblende was obtained in 1950 by Macnamara and Thode(10). These authors demonstrated that the xenon gas was not normal and was in fact radiogenic in origin as Khlopin _et al_ had suggested.

In 1953, Fleming and Thode(11) reported the relative xenon fission-product abundances in seven uranium minerals. Variations in the slopes of the fission-product mass-abundance curves, the fine structure at Xe^{134}, and the Xe^{129} abundances, indicated appreciable contributions from neutron-induced fission as well as from U^{238} spontaneous fission. It was also shown that the yield of Xe^{129} in U^{238} spontaneous fission must be very small, and that the observed Xe^{129} yields were from neutron-induced fission.

Wetherill(12), in 1953, reported the xenon and krypton pattern from a mineral having a very low Xe^{129} relative abundance, and attributed these fission products to essentially pure U^{238} spontaneous fission.

Recently the absolute yields of Mo^{99} and several iodine isotopes from U^{238} spontaneous fission were reported by Parker and Kuroda(13) and Ashizawa and Kuroda(14). In their experiments, a uranium solution was allowed to stand until the fission product reached radioactive equilibrium. Absolute abundances were obtained radiochemically on the extracted fission products, and the absolute yields were calculated on the basis of Segre's U^{238} spontaneous fission half life.

In the present work, the absolute abundances of the accumulated xenon and krypton fission products from uranium minerals were determined mass spectrometrically using the isotope-dilution technique. The purpose of this work was to obtain the absolute yields of the stable xenon and krypton fission products in U^{238} spontaneous fission, and to assess the usefulness of accumulated inert-gas fission products for age determination.

EXPERIMENTAL

Sample Preparation

The uranium minerals were crushed and sieved to provide a homogeneous aggregate for the extraction and analysis of the fission product gases.

It has been shown(15) that potassium minerals do not lose appreciable quantities of argon when crushed to 250 mesh. It was therefore assumed that uranium mineral aggregates with particle size greater than 200 mesh would not lose appreciable quantities of gas at room temperature during the period between crushing and extraction. A particle size of 60 - 200 mesh was chosen for this work to satisfy the requirements of homogeneity, negligible loss of xenon and krypton, and efficient use of the small mineral samples available.

The mineral aggregates were concentrated to a density greater than three by gravitational separation with di-iodomethane to facilitate the preparation of fission gas samples suitable for mass spectrometric analysis.

Quantitative Analysis by Isotope Dilution

Absolute isotopic abundances may be determined mass spectrometrically by means of the isotope-dilution technique.(16) A known amount of a tracer isotope of the element in question is equilibrated with the unknown mixture of isotopes. The sample, now consisting of the unknown and tracer isotopes is analyzed mass spectrometrically to determine the isotopic distribution. From the change in isotopic composition due to the addition of the tracer isotope, the absolute abundances of the isotopes in the original sample can be calculated.

A separated or synthetic stable isotope or the normal isotopic mixture may be used for the dilution of fission product xenon and krypton. Small amounts of normal xenon and krypton, however, are present in the inert gases extracted from uranium minerals. The use of a tracer containing the normal or atmospheric distribution of isotopes would therefore lead to an uncertainty in the absolute abundance determinations. Since the separated isotopes were not available, Xe^{128}, Kr^{80} and Kr^{82} were prepared by the neutron irradiation of iodine and bromine salts in the N.R.X. reactor. These isotopes occur in very low yield in fission and hence the tracer does not overlap the fission-product isotopes.

Normal xenon and krypton contain the isotopes Xe^{128}, Kr^{80} and Kr^{82} and therefore a correction must be made for the amount of normal contaminant in a sample before the absolute abundances of the fission-product isotopes can be determined. Xe^{130}, which is present in normal xenon, but occurs in very low yield in fission was used to correct for the presence of normal xenon. The normal krypton correction was made from the ratio of Kr^{80} to Kr^{82} in the tracer-diluted samples, and the corresponding ratios in the tracer and normal krypton components. In this way the normal contamination, as well as the relative and absolute abundances of fission-product xenon and krypton in a sample were determined from one mass spectrometric analysis.

Tracer Standardization

The number of atoms in a sample of the tracer may be determined by means of a gas pipette, by a calibrated Mcleod gauge, or by isotope-diluting against a standard mixture of normal xenon and krypton. The quantities of reactor-produced tracer were too small (~ 20 cu.mm.) to use the pipetting technique directly, and the tracer samples required (~ .02 cu.mm.) were considered to be too small for accurate Mcleod standardization. The numbers of atoms of Xe^{128}, Kr^{80} and Kr^{82} in a tracer sample were therefore determined by diluting against a standard mixture of normal xenon and krypton using a modification of the apparatus and techniques described by Errol, Chackett and Epstein(18).

The tracer pipetting system (Fig.3) consisted of a reservoir (R_1) and a mercury-operated gas pipette (P_1). A normal gas pipetting system consisted of a small volume (V_2), a reservoir (R_2) and a mercury-operated gas pipette (P_2). The volumes of the various components were determined before assembly. They were:-

R_1 - 5,345 ml.

R_2 - 5,445 ml.

P_1 - 3.064 ml.

P_2 - 1.098 ml.

V_2 - 1.919 ml.

A flask (F) containing 16.8% normal krypton and 83.2% normal xenon was attached to the inlet of V_2 as shown in Fig. 3. The volume v of one pipette of normal xenon and krypton at S.T.P. is:-

$$v = \frac{V_2 \times P_2}{R_2} \times \frac{P}{76} \times \frac{273}{T} \text{ ml.}$$

$$= 1.390 \frac{P}{T} \text{ ml.}$$

where P is the pressure in V_2 in cm.Hg.,

and T is the temperature of V_2 in degrees absolute.

The isotope-dilution standardization of the tracer was accomplished in the following way. The standard mixture of xenon and krypton of normal isotopic content at pressure P and temperature T from volume V_2 was expanded into the evacuated reservoir (R_2). A sample of volume v at S.T.P. was drawn off by manipulating the mercury levels of pipette P_2 and frozen onto the charcoal of a sample tube. One pipette of tracer Xe^{128}, Kr^{80} and Kr^{82} was transferred in a similar way to the same sample tube from reservoir R_1 by means of pipette P_1. The mixture of the two samples was then analyzed mass spectrometrically, and the absolute numbers of atoms of Xe^{128} and

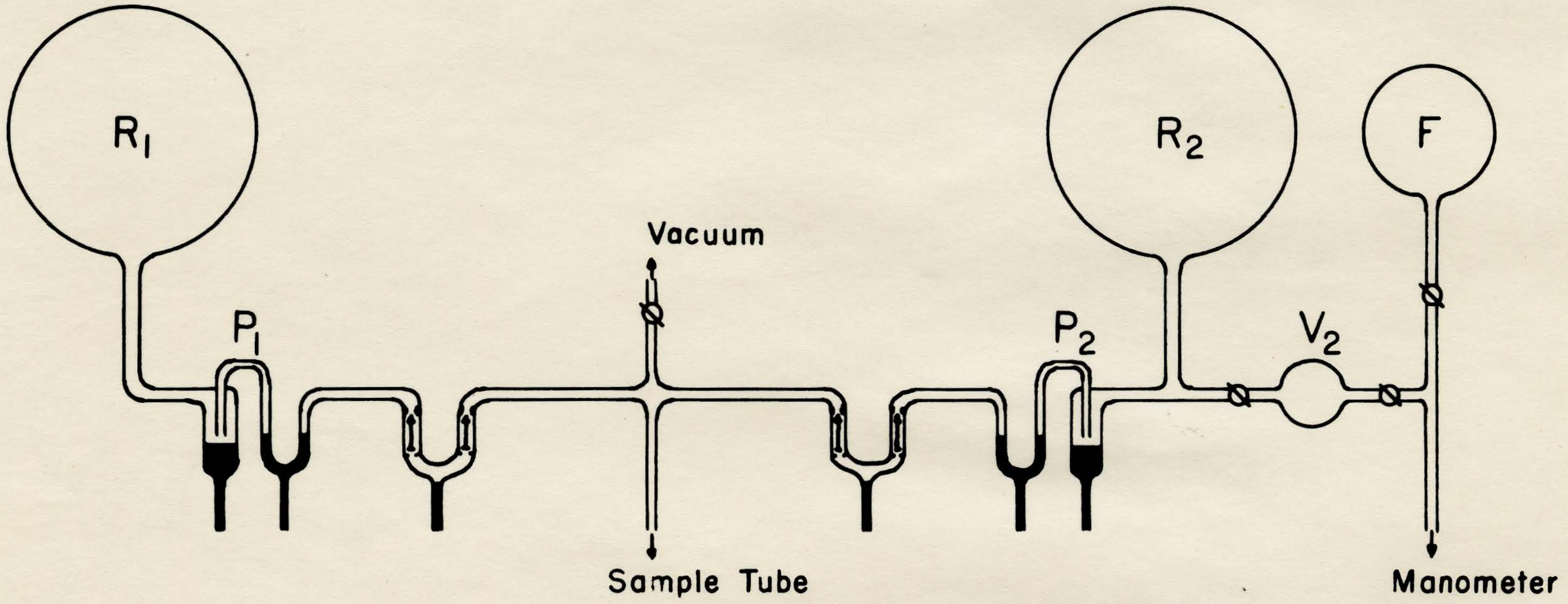

FIG. 3 GAS PIPETTING SYSTEM

Kr^{80} in the tracer sample were calculated from the changes in the normal isotopic distributions. The total number of tracer atoms in reservoir R_1 was determined from the number of atoms per pipette P_1, and the volumes of the reservoir and pipette. Thus the system was calibrated, and the number of tracer atoms in each subsequent tracer pipette volume could be calculated.

The depletion of the tracer in reservoir R_1 after each tracer pipetteful was removed could be determined more accurately from the geometry of the system than from the mass spectrometric analysis of the mixtures of normal and tracer isotopes. The precision of the standardization technique was therefore calculated from the scatter of the mass spectrometric results about the calculated rate of depletion curve.

Extraction of Fission Products from Uranium Minerals

Fleming and Thode(11) have reported the use of both dissolution and heating to remove the fission-product inert gases from minerals. They found, however, that the chemicals used in dissolution contained appreciable quantities of normal xenon and krypton which were not removed by multiple distillation, and hence recommended the heating technique. The temperatures attainable in their inconel combustion tube (1000 - 1200° C.) were sufficient to remove most of the fission-product inert gases from the minerals for relative abundance analysis. Somewhat higher temperatures (1300° C.) were necessary to remove greater than 99.5% of the inert gases in a reasonable heating period ($\sim$ eight hours) for absolute abundance analysis.

The Vacuum Induction Furnace. Temperatures up to 2000° C. could be maintained in the vacuum induction furnace shown in Fig.4. The outer envelope (A) (a four litre pyrex reaction kettle) was sealed to a water cooled brass base (B) by means of a neoprene 'O' ring. A pyrex crucible holder (C) contained three concentric graphite shells (D) surrounded by lamp black refractory (E). The graphite shells absorbed radio-frequency power from the tank coil (F). The crucible (G) which contained the crushed mineral concentrate was formed from .005" molybdenum. A molybdenum radiation shield (J) over the gas port (K) reduced radiation losses.

A six kilowatt Ajax Northrup mercury-arc converter supplied the radio-frequency power to the coil. The output from this supply could be varied only within narrow limits. Therefore the furnace temperature was maintained at a constant level during the eight-hour heating period by cycling the power on and off with a 30-second period. The temperature control device, consisting of a one r.p.m. synchronous motor driving two cam-operated microswitches is shown schematically in Fig.5. The percentage of the 30 second period during which power was supplied to the coil could be continuously varied from zero to 100% by altering the relative angular positions of the two cams.

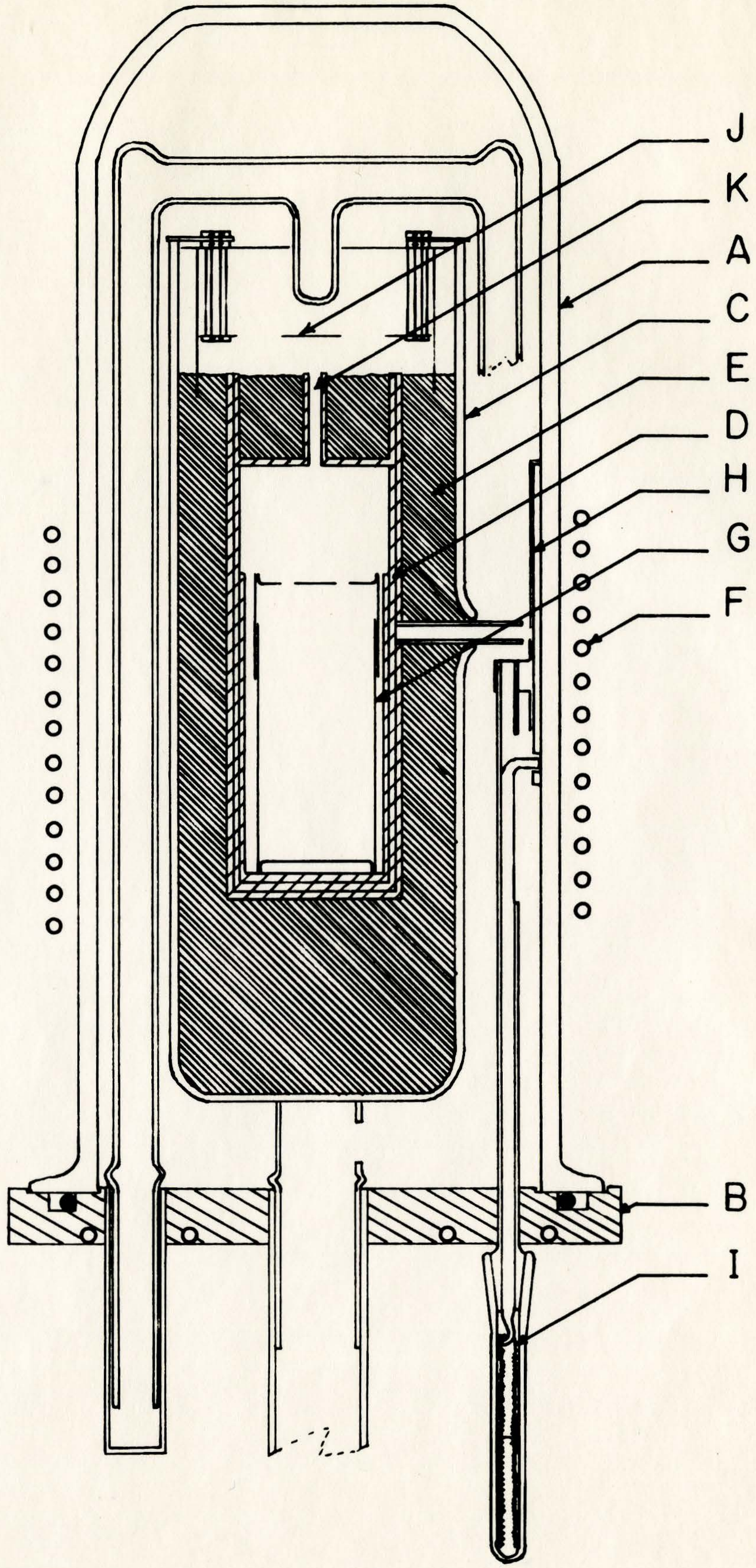

FIG. 4 VACUUM INDUCTION FURNACE

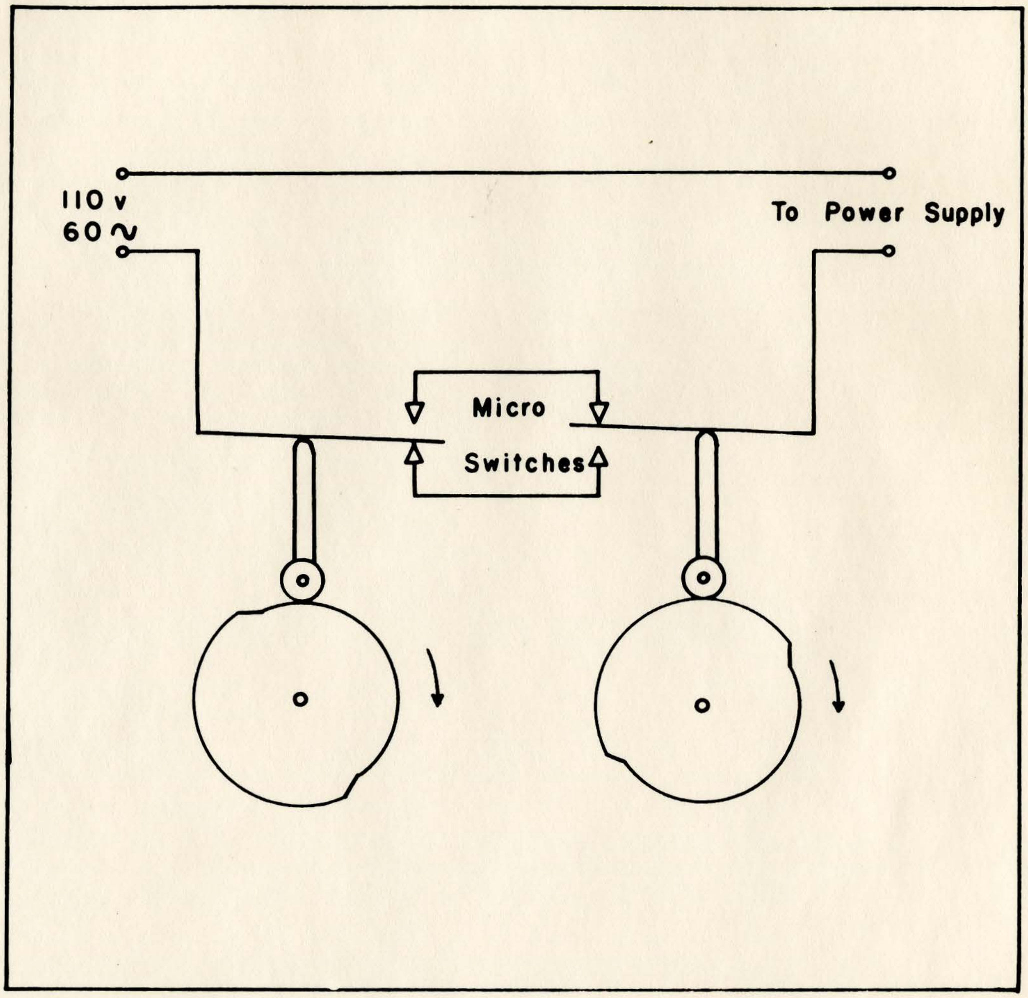

FIG. 5 INDUCTION FURNACE POWER CONTROL

The furnace temperature was measured by means of a Leeds and Northrup optical pyrometer which was focused on the middle graphite shell. Gases evolved from the heated mineral condensed on the inside of the furnace envelope, however, and made optical temperature measurements unreliable. In order to make accurate optical temperature measurements under these conditions, a glass slide was mounted inside a molybdenum shield (H) in front of the viewing port. When this inner glass became clouded it was drawn down by a screw and ground glass joint arrangement (I) to expose a clean portion of the slide.

Extraction Procedure. The furnace was baked for several hours at about 1700° C. under high vacuum before charging with the mineral sample in order to remove any xenon and krypton which might be absorbed in the lamp black or graphite. After cooling, the furnace compartment was raised to atmospheric pressure with nitrogen, charged with about 100 grams of the crushed mineral concentrate, and outgassed under high vacuum at room temperature for about 36 hours to remove adsorbed normal xenon and krypton from the mineral. The furnace compartment was then isolated and the temperature was raised slowly to 1300° C. and held at this temperature for eight hours. The evolved gases were mixed with tracer, separated and purified according to the techniques to be described in the following section. In order to test the completeness of the extraction, the mineral was reheated to about 1400° C. for eight hours. The evolved gases were again mixed with tracer, separated and purified. The extraction was considered complete if the reheat fission products were less than 0.5% of those found in the first heat.

The Separation and Purification of the Tracer-Fission Product Mixture

Approximately 15 litres of gas were evolved from 100 grams of pitchblende. This gas was predominantly carbon monoxide, with small quantities of helium and water vapour, and trace amounts of fission product xenon and krypton. The apparatus used to remove .0001 ml. of xenon and krypton from the evolved gases is shown schematically in Fig.6. Traps T_1 and T_2 were open and traps C_1 and C_2 contained activated charcoal. A 25 litre reservoir was connected at the points shown. The purification section, which consisted of a charcoal trap (C_3) and a calcium induction furnace, could be isolated by means of mercury ventils.

Admission of Tracer to the Reservoir. Furnace gas was introduced into the evacuated space above the break seal of the tracer sample tube. After the seal was broken, the furnace gas was mixed with the tracer by heating the sample tube to about 600° C. The tracer-furnace gas mixture was then expanded into the evacuated 25 litre reservoir. This flushing procedure was repeated three times before sealing off the tracer tube and transferring the remaining furnace gas into the

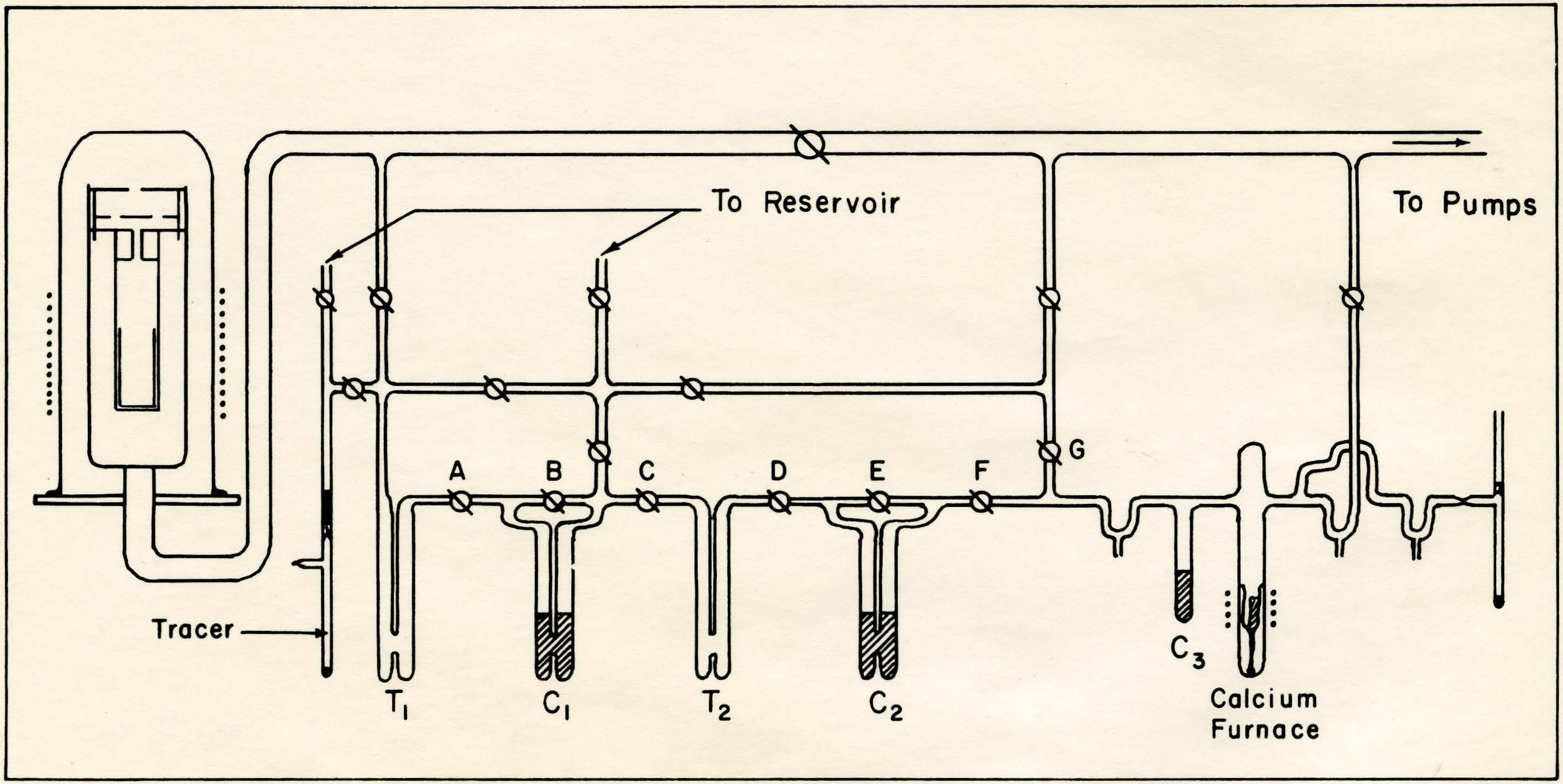

FIG. 6 INERT GAS SEPARATION SYSTEM

reservoir. The eight hour heating period, during which the evolved gas was periodically admitted to the reservoir, ensured equilibration of tracer and fission-product gases.

Separation Procedure. Since the tracer was mixed with all of the gas which was removed from the mineral sample, substantial losses of the tracer-fission product mixture could be tolerated without introducing error into the absolute abundance measurements. Preliminary tests indicated that separation losses did not exceed 5% for xenon or 10% for krypton.

Two litre portions of reservoir gas were pumped slowly through T_1, C_1, T_2 and C_2 at liquid nitrogen temperature. Water and carbon dioxide were removed in trap T_1. Xenon, krypton and carbon monoxide were adsorbed on the charcoal of traps C_1 and C_2. Helium was pumped through. Stopcocks A, B, and E (Fig.6) were then closed, and traps C_1 and C_2 were warmed slowly to -80° C. by means of a dry ice and acetone bath. During the warming most of the carbon monoxide was pumped off, leaving a residue which was enriched in xenon and krypton. The enriched residue was transferred to charcoal trap C_3 in the purification section.

Purification Procedure. When most of the reservoir xenon and krypton had been separated and transferred to trap C_3, it was purified by reacting all but the inert gases with calcium vapour in the calcium induction furnace. It was found that the purification rate was greatest when the gas was maintained at a pressure which would support a strong discharge, and the calcium temperature was kept just below its melting point. The purified inert gases were removed in a sample tube for mass spectrometric analysis.

Mass Spectrometry

The inert gas mixtures were analyzed on a 10" directional focusing mass spectrometer using an electron multiplier for a detector. The multiplier output was integrated and amplified by a vibrating reed electrometer and displayed on a recorder. A resolving power of about 625 allowed doublet separation of the hydrocarbon background from the xenon and krypton isotopes.

The samples were admitted to the mass spectrometer leak through mercury ventils to reduce absorption of the inert gases in stopcock grease and to reduce the hydrocarbon background. Liquid nitrogen was placed on a capillary trap in front of the gas leak before the sample was introduced. In this way the xenon was condensed in the trap and held there during the krypton scanning. The trap was warmed to -80° C. for xenon scanning. Any impurities which might be present in the sample were therefore not admitted to the leak unless they had appreciable vapour pressures at -80° C. for xenon and -180° C. for krypton.

The instrument had a long term memory for xenon and could reproduce a very weak xenon spectrum weeks after the sample had been pumped out. The cause of this memory effect was not definitely established. It was found, however, that flushing with neon for 15 minutes with the liquid air trap warmed to -80° C. and subsequent pumping for eight hours reduced this effect to a negligible level compared to the ion currents produced by the fission product samples.

The vibrating reed shunt resistances and the external shunt resistances were calibrated by means of a student potentiometer and constant voltage source before and after each set of analyses. In all cases the shunt resistances had the nominal values within the 0.2% reproducibility of the calibration procedure.

Mass Discrimination Correction. Several of the mass spectrometer components, including the electron multiplier, gas leak, and ion source, may introduce a mass dependence into isotope abundance measurements. A sample of normal xenon and krypton, approximately equal in size to the fission-product samples, was therefore analyzed before and after each set of fission-product analyses. The instrument settings and measuring techniques were the same for the normal and fission-product analyses. When the measured normal isotopic abundances were compared with those reported by Nier(19), a linear deviation was noted. This deviation favoured the light isotopes by about 3% and 2% over the mass ranges 80-86 and 128-136 respectively, and was attributed to instrumental mass discrimination. A correction for this effect was therefore applied to all abundance measurements.

Chemical Analysis.

Method number one in the "Manual of Analytical Methods for the Determination of Uranium and Thorium in their Ores," published by the United States Atomic Energy Commission, was used to measure the uranium concentration in the six minerals.

The mineral was dissolved by a treatment with nitric and sulphuric acids. The hydrogen sulphide group was removed, and a cupferron precipitation was made to further remove interfering elements. Nitric acid was removed and organic matter was destroyed by fuming with sulphuric acid. The uranium solution was then reduced in a Jones reductor. After reduction the solution was aerated to oxidize any trivalent uranium to the tetravalent state. Potassium dichromate was used for the titration.

Blank titrations were run on dilute sulphuric acid which had been reduced in the Jones reductor and aerated. A standard solution of uranium nitrate was prepared from a weighed sample of fuel rod uranium, and was used to test the analytical procedures. The uranium mineral titrations were corrected for the results of the blank and standard solution titrations.

Two analyses were performed on each mineral, starting from crushed concentrates which were sampled from the same aggregates as those used for fission-product analyses.

RESULTS

Tracer Standardization

The techniques described above were used to draw off 38 tracer samples. The first two samples of each set of 12 were standardized by adding a known quantity of the standard mixture of normal xenon and krypton isotopes. The number of atoms of Xe^{128} and Kr^{80} in each of the eight standardization mixtures (tracer samples 1, 2, 13, 14, 25, 26, 37, 38) is shown in Table 1. The precision of these eight results is the standard deviation from four double mass spectrometer scans. The depletion of the amount of gas in reservoirs R_1 and R_2 during the removal of the 38 samples was calculated from the geometry of the system to be 0.14% and 2.18%, respectively. By fitting the rate of depletion curve to the eight standardized tracer abundances, the number of tracer atoms in each of the pure tracer samples was calculated. These samples (3-12, 15-24, 27-36) were used for the isotope dilution of the gases extracted from uranium mineral samples. The scatter of the eight results about the calculated depletion curve was found to be ± 0.32% and ± 0.88% for Xe^{128} and Kr^{80} respectively. The mass spectrometer standard deviation (± 0.28% and ± 0.80% for Xe^{128} and Kr^{80} respectively) indicated that the reproducibility of the standardization procedure was limited by the mass spectrometric analysis, rather than

TABLE I

TRACER STANDARDIZATION

Tracer Sample No.	Xe^{128} Atoms ($\times 10^{14}$)	Kr^{80} Atoms ($\times 10^{13}$)	Tracer Sample No.	Xe^{128} Atoms ($\times 10^{14}$)	Kr^{80} Atoms ($\times 10^{13}$)
1	5·98 ± ·02	8·29 ± ·06	20	5·91	8·25
2	5·99 ± ·01	8·26 ± ·05	21	5·91	8·25
3	5·97	8·33	22	5·90	8·24
4	5·97	8·33	23	5·90	8·24
5	5·97	8·32	24	5·90	8·23
6	5·96	8·32	25	5·88 ± ·01	8·18 ± ·04
7	5·96	8·31	26	5·88 ± ·02	8·18 ± ·05
8	5·96	8·31	27	5·89	8·22
9	5·95	8·30	28	5·88	8·22
10	5·95	8·30	29	5·88	8·21
11	5·94	8·29	30	5·88	8·20
12	5·94	8·29	31	5·87	8·20
13	5·91 ± ·02	8·29 ± ·04	32	5·87	8·20
14	5·94 ± ·01	8·43 ± ·12	33	5·86	8·19
15	5·93	8·27	34	5·86	8·19
16	5·93	8·27	35	5·86	8·18
17	5·92	8·26	36	5·86	8·18
18	5·92	8·26	37	5·86 ± ·01	8·19 ± ·03
19	5·92	8·26	38	5·88 ± ·02	8·21 ± ·05

Xe^{128} Standardization Precision = $\pm \cdot 02 \times 10^{14}$

Kr^{80} Standardization Precision = $\pm \cdot 07 \times 10^{13}$

the pipetting technique or the equilibration of the tracer normal mixtures.

The ratio of Kr^{80} to Kr^{82} in the krypton tracer was found to be 3.718 ± .015.

Mineral Age and Uranium Content

The results of the lead age determination and the uranium analyses on the six uranium minerals are given in Table II.

The mineral ages were obtained from the radiogenic Pb^{207}: Pb^{206} ratio by Farquhar and others of the Geophysics group at the University of Toronto. The Cinch Lake and Beaverlodge Lake ages were determined from samples of the minerals used for the fission-product analysis. The remaining ages were determined on samples obtained from the same mineral deposits.

Isotopic Abundances of Xenon and Krypton Fission Products

Analyses based on the primary mass spectrometric data may be divided into two parts. Relative xenon isotopic abundances only are required for the normal xenon correction and for analysis of the fission products into their components. Absolute abundances, however, are necessary to determine absolute yields and to measure any loss of fission product gas from the mineral. The precision of the relative xenon fission product abundances depends only on the reproducibility of the mass spectrometric data and the accuracy with which the normal contamination correction can be made. The precision of the absolute xenon and krypton abundances or of the krypton

TABLE II

MINERAL AGE AND URANIUM CONTENT

Mineral	Cinch Lake Pitchblende	Jahala Lake Uraninite	Beaverlodge Lake Pitchblende	Great Bear Lake Pitchblende	Eagle Mine Pitchblende	Belgian Congo Pitchblende
Lead Age (x10^6 y) (Ref.)	1120 ± 50 (20)	1740 ± 50 (15)	785 ± 60 (20)	1400 ± 50 (21)	1700 ± 30 (22)	635 ± 20 (21)
U^{238} (%)	29·0 ± ·3	30·4 ± ·4	41·2 ± 1·4	43·3 ± ·4	45·3 ± ·4	56·4 ± ·5
Sample Wt. (g)	65·1	128·0	103·8	69·7	99·5	115·3

relative to xenon is somewhat lower, however, since it includes, in addition, the reproducibility of the tracer standardization and the ratio of tracer to fission-product abundances.

The relative and absolute abundances were normalized to 100 at Xe^{136} for comparison, and are shown in Tables III and IV respectively. The Xe^{129} abundance relative to Xe^{136} is considered to be a good indication of the percentage of neutron fission in the mineral, and hence the minerals were arranged in order of increasing Xe^{129} abundance. The normal contamination corrections are shown in the lower part of Table III. The precision indices are the standard deviations based on seven mass spectrometer double scans.

The complete extraction criterion (99.5%) suggested in the Extraction Procedure was satisfied for four of the six minerals. The Jahala Lake and Belgian Congo reheats, however, produced fission products which were 1.4% and 4%, respectively, of the first heat abundances. Although reheat corrections were applied, the absolute abundances from these two minerals cannot be considered as reliable as those from the other four.

In order to test the reproducibility of the isotope dilution and mass spectrometric techniques, two samples of the same Great Bear Lake aggregate were analyzed for fission product xenon and krypton with a six month interval between the analyses. The good agreement between the two sets of data shown in Table V suggests not only that the results are reproducible within experimental error, but that non-inert gas

TABLE III

RELATIVE ABUNDANCES OF Xe FISSION PRODUCTS

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Xe^{129}	0·460 ± ·019	0·488 ± ·007	0·800 ± ·073	2·06 ± ·02	2·29 ± ·02	3·38 ± ·03
Xe^{131}	9·88 ± ·03	9·77 ± ·05	11·41 ± ·10	15·43 ± ·05	15·85 ± ·09	20·51 ± ·08
Xe^{132}	57·97 ± ·08	58·18 ± ·20	58·44 ± ·18	59·76 ± ·11	59·05 ± ·18	61·39 ± ·19
Xe^{134}	83·36 ± ·05	83·72 ± ·18	85·27 ± ·13	89·17 ± ·11	89·83 ± ·21	94·46 ± ·14
Xe^{136}	100·00 ± ·08	100·00 ± ·23	100·00 ± ·18	100·00 ± ·13	100·00 ± ·21	100·00 ± ·19
$\frac{\text{Normal Kr}}{\text{Fission Kr}}$	·130	·640	·440	·096	·180	·082
$\frac{\text{Normal Xe}}{\text{Fission Xe}}$	·0094	·0050	·0240	·0061	·0055	·0066

TABLE IV

ABSOLUTE ABUNDANCES OF Xe AND Kr FISSION PRODUCTS

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Kr^{83}	0·854 ± ·030	0·728 ± ·022	0·865 ± ·044	1·71 ± ·02	1·75 ± ·05	2·56 ± ·03
Kr^{84}	2·52 ± ·15	2·45 ± ·09	1·98 ± ·21	3·94 ± ·09	4·23 ± ·18	5·40 ± ·13
Kr^{86}	15·79 ± ·21	12·54 ± ·15	14·37 ± ·18	16·49 ± ·17	15·43 ± ·20	17·95 ± ·20
Xe^{129}	0·460 ± ·021	0·488 ± ·009	0·800 ± ·073	2·06 ± ·01	2·29 ± ·02	3·38 ± ·02
Xe^{131}	9·88 ± ·06	9·77 ± ·07	11·41 ± ·11	15·43 ± ·12	15·85 ± ·11	20·51 ± ·15
Xe^{132}	57·97 ± ·27	58·18 ± ·48	58·44 ± ·33	59·76 ± ·43	59·05 ± ·59	61·39 ± ·37
Xe^{134}	83·36 ± ·36	83·72 ± ·63	85·27 ± ·38	89·17 ± ·75	89·83 ± ·84	94·46 ± ·50
Xe^{136}	100·00 ± ·42	100·00 ± ·94	100·00 ± ·41	100·00 ± ·95	100·00 ± ·83	100·00 ± ·65
Xe^{136} Atoms ($\times 10^{14}$)	3·312	7·710	1·352	6·033	7639	4·838

TABLE V

REPRODUCIBILITY OF ABSOLUTE ABUNDANCE MEASUREMENTS

(Great Bear Lake Pitchblende)

Fission Product	Sample No. 1	Sample No. 2
Kr^{83}	1·75 ± ·05	1·71 ± ·02
Kr^{84}	4·40 ± ·25	3·94 ± ·09
Kr^{86}	16·40 ± ·31	16·49 ± ·17
Xe^{129}	1·98 ± ·34	2·06 ± ·01
Xe^{131}	15·54 ± ·31	15·43 ± ·11
Xe^{132}	59·69 ± ·62	59·76 ± ·39
Xe^{134}	89·08 ± ·92	89·17 ± ·68
Xe^{136}	100·0 ± 1·4	100·00 ± ·88
Xe^{136} Atoms per 100 Grams of Sample	$8{\cdot}51 \times 10^{14}$	$8{\cdot}65 \times 10^{14}$

contamination and mass spectrometric memory effects are negligible, since these should not be the same for the two analyses.

<u>The Number of U^{238} Spontaneous Fissions in a Mineral Sample</u>. The absolute yield calculation depends on the independent determination of the number of fissions which have taken place, and the amount of a given fission product which has been formed.

The total number of U^{238} atoms which have undergone spontaneous fission in a mineral sample since deposition may be calculated from the U^{238} content, the age, and the rates at which the U^{238} nucleus decays by alpha-emission and spontaneous fission. It can be shown that the total number (N) of U^{238} spontaneous fissions is given by:

$$N = W \frac{\lambda_f}{\lambda_\alpha} \left[e^{\lambda_\alpha T} - 1 \right] \quad , \ldots\ldots\ldots \ (1)$$

where W = the present number of U^{238} atoms in the mineral sample (Table II),

λ_f = the U^{238} spontaneous fission decay constant $= 8.62 \pm .30 \times 10^{-17}/y$ (8),

λ_α = the U^{238} alpha decay constant $= 1.54 \times 10^{-10}/y$ (23),

T = the period during which fission products accumulated.

The spontaneous fission decay rate in normal uranium has been reported by several workers(8)(24-29). Of these, only Segre(8) determined the decay rate of U^{238} separately, and hence his value was used for λ_f.

The period during which fission products accumulated was assumed to be that given by the 'lead-lead' age (Table II).

The number of U^{238} atoms which have undergone fission was calculated for each of the six mineral samples from equation (1) and is shown, together with the lead age and uranium content in Table VI.

Isotopic Abundances of Xenon and Krypton from the Spontaneous Fission of U^{238}

The spontaneous fission of the U^{238} nucleus is independent of external factors and must result in a unique mass distribution of fission products. The variations among the isotope patterns from the six uranium minerals therefore indicated that processes other than U^{238} spontaneous fission had contributed xenon and krypton isotopes. The analyses to be described attempted to identify these processes and to correct for their contributions to the measured xenon and krypton isotopic abundances. The criterion for a satisfactory analysis was that the fission-product patterns from the six minerals must agree within experimental error after the corrections were applied.

The relative abundances of the xenon isotopes were used for these analyses for several reasons. First, these abundances were more accurately determined than the abundances of the

TABLE VI

SPONTANEOUS FISSION DATA

Mineral	U^{238} Content (Grams)	Lead Age ($\times 10^9$ Years)	U^{238} Spontaneous Fissions ($\times 10^{16}$)
Cinch Lake	18·9 ± ·2	1·12 ± ·05	0·503 ± ·030
Jahala Lake	38·9 ± ·5	1·74 ± ·05	1·69 ± ·07
Beaverlodge Lake	42·8 ± 1·5	0·78 ± ·06	0·78 ± ·13
Great Bear Lake	30·2 ± ·3	1·40 ± ·05	1·03 ± ·05
Eagle Mine	45·1 ± ·4	1·70 ± ·03	1·91 ± ·08
Belgian Congo	65·0 ± ·6	0·64 ± ·02	0·94 ± ·05

krypton isotopes relative to the xenon isotopes. Also, it is possible that some inert gases might have been lost from the minerals and that a fractionation of krypton relative to xenon might have accompanied these losses. Finally, the five stable xenon isotopes are sufficient for an analysis into several components, and for a check on the validity of the analysis.

The 129 Mass Chain Relative Abundance. The unstable precursors to the stable xenon and krypton fission products have with one exception half lives which are short relative to geological periods of the order of 10^9 years. The exception, I^{129}, decays with a half life of 1.72 ± .09 x 10^7 years(30) to stable Xe^{129}. Part of the 129 mass chain must therefore be present as I^{129} at the time of extraction. Fleming and Thode(11) have shown that the 129 mass chain in natural uranium fission is fed mainly by U^{235} neutron fission. If it is assumed that the neutrons which induce U^{235} neutron fission have a constant energy distribution and flux throughout geological time, then it can be shown that the ratio of I^{129} to the accumulated mass chain yield is given by:

$$\frac{I^{129}}{I^{129} + Xe^{129}} = \frac{\lambda_{U^{235}} \left(e^{-\lambda_{U^{235}}T} - e^{-\lambda_{I^{129}}T}\right)}{\left(\lambda_{I^{129}} - \lambda_{U^{235}}\right)\left(1-e^{-\lambda_{U^{235}}T}\right)}, \quad \ldots\ldots(2)$$

where $\lambda_{U^{235}}$ = the U^{235} alpha decay constant
$= 9.72 \times 10^{-10}/y$ (31),

$\lambda_{I^{129}}$ = the I^{129} beta decay constant
$= 4.08 \times 10^{-8}/y$ (30),

T is the period during which fission products accumulated.

The percentage of the 129 mass chain which remained as I^{129} in each of the various minerals at the time of extraction is given in Table VII together with the total 129 mass chain relative abundance. These corrected abundances were used for the analyses of the measured patterns into their components.

Xenon Contribution from Processes other than the Spontaneous Fission of U^{238}. It was mentioned in the Introduction that only U^{238} could contribute appreciable spontaneous fission products in uranium minerals. Also, no alpha, beta or gamma induced reactions are known which could have produced discernable xenon isotopes. Neutrons, however, which result from fission, (α,n) reactions, and cosmic rays could have induced reactions which might have contributed xenon contaminants. Among such possible reactions the following six are most important:

(1) $U^{235}\ (n,f) \longrightarrow$ xenon fission products

(2) $U^{238}\ (n,f) \longrightarrow$ xenon fission products

(3) $Th^{232}\ (n,f) \longrightarrow$ xenon fission products

(4) $Te^{128}\ (n,\gamma)\ Te^{129} \longrightarrow I^{129} \longrightarrow Xe^{129}$

TABLE VII

THE 129 MASS-CHAIN RELATIVE ABUNDANCE

Mineral	Xe^{129} (Measured)	$\frac{I^{129}}{Xe^{129}+I^{129}}\times 100$	Xe^{129} † (Corrected)
Cinch Lake	0·460 ± ·019	1·4	0·466 ± ·019
Jahala Lake	0·488 ± ·007	0·6	0·491 ± ·007
Beaverlodge Lake	0·800 ± ·075	2·1	0·818 ± ·075
Great Bear Lake	2·06 ± ·02	0·9	2·08 ± ·02
Eagle Mine	2·29 ± ·02	0·6	2·30 ± ·02
Belgian Congo	3·38 ± ·03	3·1	3·48 ± ·03

† Corrected to give the total abundance of the 129 mass-chain

(5) $Te^{130}\ (n,\gamma)\ Te^{131} \longrightarrow I^{131} \longrightarrow Xe^{131}$

(6) $Ba^{130}\ (n,\gamma)\ Ba^{131} \longrightarrow Cs^{131} \longrightarrow Xe^{131}$

Since thorium, tellurium and barium are not common contaminants in uranium minerals, it was assumed that xenon contributions from neutron reactions with these nuclides were negligibly small. The validity of these assumptions will be considered in more detail in the Discussion.

Wanless and Thode(32) reported the relative isotopic abundances of the xenon and krypton fission products from the thermal neutron-induced fission of U^{235} and the fast neutron-induced fission of U^{238}. The absolute yields of the xenon and krypton isotopes from these two fission processes were obtained by fitting the relative yields to their respective mass-yield curves(33)(34)(35).

Table VIII presents the relative yields in the neutron fission of U^{235} and U^{238} normalized to 100 at Xe^{136} for comparison. The errors are the standard deviations for the relative yield determinations. Included in Table VIII are the relative yield of I^{129} in U^{235} thermal neutron fission from the work of Purkayastha and Martin(36) and the 129 chain yield interpolated from the mass-yield curve of U^{238} neutron fission. Since Xe^{129} is known to have a very small primary yield in U^{235} thermal neutron fission(3), the cumulative yield to I^{129} may be used as the total yield for the 129 mass chain.

TABLE VIII

RELATIVE YIELDS OF FISSION PRODUCTS IN NEUTRON-INDUCED FISSION OF U^{235} AND U^{238}

Fission Product	U^{235} Thermal Neutron Fission	U^{238} Fast Fission
Kr^{83}	8·4 ± ·0	6·9 ± ·3
Kr^{84}	15·5 ± ·1	14·4 ± ·7
Kr^{86}	31·3 ± ·1	23·4 ± ·5
I^{129}	13·9	(13·6) †
Xe^{131}	45·34 ± ·25	54·60 ± ·45
Xe^{132}	67·86 ± ·26	80·06 ± ·45
Xe^{134}	124·72 ± ·26	112·68 ± ·49
Xe^{136}	100·00 ± ·41	100·00 ± ·38

† Interpolated from the Mass-Yield Curve

Fission-Product Analysis Based on Xe^{129}. Fleming and Thode(11) showed that the Xe^{129} yield in U^{238} spontaneous fission was very small, and attributed the observed Xe^{129} abundances in uranium minerals to U^{235} neutron fission. A preliminary analysis was therefore attempted by assuming that the mineral patterns were mixtures of fission products from U^{235} neutron fission and U^{238} spontaneous fission in which the Xe^{129} abundances were from U^{235} neutron fission alone. The six mineral patterns corrected for the U^{235} neutron fission component by means of the Xe^{129} relative abundances and renormalized to 100 at Xe^{136}, are shown in Table IX. The discrepancies among the xenon abundances observed in Table III were partially removed, but the analysis is obviously incomplete. The correlation between the corrected xenon abundances and the amount of neutron fission suggests that an undercorrection has been made for the neutron component. Since this apparent undercorrection could result from the use of a Xe^{129} yield in U^{235} neutron fission which was too large, an analysis was attempted in which the correction for the neutron component was independent of this yield.

Fission-Product Analysis Based on Xe^{134} and Xe^{136}. The Cinch Lake xenon pattern contains the smallest amount of neutron fission and is therefore a first approximation to the U^{238} spontaneous fission pattern. A comparison of this pattern with that from U^{235} thermal neutron fission showed that the ratios of Xe^{134} to Xe^{136} differed by about 40%. Therefore a

TABLE IX

FISSION-PRODUCT PATTERNS CORRECTED FOR NEUTRON FISSION

(Correction Based on Xe^{129})

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Kr^{83}	0·592 ± ·030	0·447 ± ·023	0·393 ± ·047	0·53 ± ·02	0·47 ± ·06	0·64 ± ·04
Kr^{84}	2·07 ± ·15	1·97 ± ·09	1·14 ± ·22	1·90 ± ·11	2·03 ± ·22	2·13 ± ·17
Kr^{86}	15·26 ± ·12	11·77 ± ·16	13·31 ± ·19	13·89 ± ·20	12·47 ± ·24	13·78 ± ·27
Xe^{129}	0·000 ± ·019	0·000 ± ·007	0·000 ± ·075	0·00 ± ·02	0·00 ± ·02	0·00 ± ·03
Xe^{131}	8·65 ± ·07	8·47 ± ·05	9·30 ± ·27	10·17 ± ·11	10·01 ± ·13	12·22 ± ·17
Xe^{132}	57·63 ± ·12	57·82 ± ·21	57·85 ± ·40	58·34 ± ·18	57·30 ± ·25	59·23 ± ·32
Xe^{134}	81·92 ± ·19	82·21 ± ·20	82·81 ± ·71	82·91 ± ·25	82·91 ± ·34	84·36 ± ·40
Xe^{136}	100·00 ± ·17	100·00 ± ·24	100·00 ± ·57	100·00 ± ·24	100·00 ± ·30	100·00 ± ·39
Xe^{136} (%) from U^{238} S.F.	96·65	96·47	94·12	85·04	83·45	74·96

two component analysis on the other five mineral patterns was made from the ratios of Xe^{134} to Xe^{136}. A relative yield of Xe^{129} in U^{235} neutron fission was then obtained from each of the five mineral patterns by comparing the Xe^{129} abundance, assumed to be from U^{235} fission alone, with the portion of the Xe^{136} abundance which the analysis indicated was from U^{235} neutron fission. The average of these five relative yield determinations was used to correct the Cinch Lake pattern for its neutron fission contribution, and thus obtain a second approximation to the U^{238} spontaneous fission pattern. This successive approximation procedure was repeated until internal Xe^{129} consistency was achieved. The Xe^{129} yield in U^{235} neutron fission was found to be 11.51 ± .37% of the Xe^{136} yield and was therefore about 20% lower than the value obtained by Purkayastha and Martin.

The corrected xenon and krypton patterns from the six minerals are given in Table X along with the percentage contributions of Xe^{136} from U^{238} spontaneous fission to the measured Xe^{136} abundances. The corrected patterns are seen to be in better agreement than those from the first analysis, but do not agree within the precision of measurement. The corrected Xe^{131} abundances, and to a lesser extent, the Xe^{132} abundances, increase with increasing neutron fission. It is evident from this analysis that it is not possible to separate the six mineral patterns uniquely into a U^{235} neutron fission component and a U^{238} spontaneous fission component.

TABLE X

FISSION-PRODUCT PATTERNS CORRECTED FOR NEUTRON FISSION

(Correction Based on Xe^{134} and Xe^{136})

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Kr^{83}	0·535 ± ·035	0·332 ± ·023	0·164 ± ·048	0·28 ± ·02	0·17 ± ·06	0·07 ± ·06
Kr^{84}	1·97 ± ·16	1·78 ± ·09	0·72 ± ·23	1·48 ± ·11	1·57 ± ·22	1·11 ± ·19
Kr^{86}	15·13 ± ·23	11·48 ± ·16	12·80 ± ·20	13·34 ± ·21	11·69 ± ·25	12·28 ± ·28
Xe^{129}	0·000 ± ·032	- 0·075 ± ·020	- 0·174 ± ·089	+ 0·07 ± ·07	+ 0·14 ± ·07	+ 0·09 ± ·16
Xe^{131}	8·38 ± ·10	7·94 ± ·05	8·26 ± ·10	9·07 ± ·08	8·90 ± ·12	9·96 ± ·12
Xe^{132}	57·55 ± ·28	57·68 ± ·21	57·73 ± ·20	58·03 ± ·15	56·97 ± ·23	58·64 ± ·30
Xe^{134}	81·61 ± ·27	81·61 ± ·19	81·61 ± ·14	81·61 ± ·15	81·61 ± ·26	81·61 ± ·23
Xe^{136}	100·00 ± ·23	100·00 ± ·24	100·00 ± ·20	100·00 ± ·18	100·00 ± ·27	100·00 ± ·31
Xe^{136} (%) from U^{238} S.F.	95·95	95·11	91·51	82·47	80·93	70·19

Fission-Product Analysis on Xe^{131}, Xe^{134} and Xe^{136}. The preceding analyses neglected the possibility of fission-product contributions from U^{238} neutron induced fission. It can be seen from Table VIII, however, that the Xe^{131} relative yield in U^{238} neutron fission is about 20% higher than in U^{235} neutron fission. The neglect of this third kind of fission could therefore account qualitatively for the Xe^{131} discrepancy in the second analysis. A quantitative test of this possibility was made by analyzing the patterns from the six uranium minerals into three components using the measured Xe^{131}, Xe^{134} and Xe^{136} relative abundances and the corresponding relative yields in the three kinds of fission. The successive approximation procedure adopted in the second analysis was also used here to obtain the U^{238} spontaneous fission pattern and an effective Xe^{129} yield for the two neutron fission components. The relative Xe^{129} yields from U^{235} and U^{238} neutron induced fission were assumed to be equal. This assumption will be considered further in the Discussion. The weighted mean of the ratio

$\frac{Xe^{129}}{Xe^{136}}$ x 100 for the neutron components of the five minerals

other than Cinch Lake was found to be 11.1 ± .3. It was assumed that the neutron fission component in the Cinch

Lake mineral arose from U^{235} neutron-induced fission alone. It can be shown, however, that the neglect of 20% U^{238} neutron-induced fission in the neutron fission component of the Cinch Lake mineral could not alter the corrected fission-product relative abundances beyond experimental error.

The corrected xenon and krypton patterns from the six minerals are shown in Table XI. This analysis is seen to be quite satisfactory. The scatter of the Xe^{129} residual about zero is somewhat larger than the precision of measurement for three of the six minerals, and the Xe^{132} corrected abundance from Eagle Mine pitchblende is low by about twice the standard deviation. However, all the remaining corrected abundances agree within the precision of measurement.

The percentage contributions from the three fission components and the ratio of Xe^{129} to Xe^{136} for the neutron induced fission component are shown in Table XII for each of the six mineral samples.

The Absolute Yields of Xenon and Krypton Isotopes in the Spontaneous Fission of U^{238}.

The number of U^{238} spontaneous fissions and the amounts of xenon and krypton fission products from U^{238} spontaneous fission have been determined for each of the six uranium minerals. The ratio of the absolute abundance of one of the spontaneous fission products, e.g. Xe^{136}, to the number of

TABLE XI

FISSION-PRODUCT PATTERNS CORRECTED FOR NEUTRON FISSION

(Correction Based on Xe^{131}, Xe^{134} and Xe^{136})

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Kr^{83}	0·519 ± ·031	0·412 ± ·023	0·175 ± ·048	0·25 ± ·02	0·15 ± ·06	0·00 ± ·06
Kr^{84}	1·94 ± ·16	1·92 ± ·09	0·74 ± ·23	1·36 ± ·11	1·47 ± ·22	0·85 ± ·20
Kr^{86}	15·10 ± ·22	11·68 ± ·16	12·82 ± ·20	13·41 ± ·21	11·73 ± ·25	12·46 ± ·29
Xe^{129}	0·000 ± ·019	+ 0·060 ± ·015	- 0·113 ± ·086	+ 0·06 ± ·06	+ 0·15 ± ·06	+ 0·01 ± ·13
Xe^{131}	8·31 ± ·10	8·31 ± ·05	8·31 ± ·11	8·31 ± ·07	8·31 ± ·12	8·31 ± ·16
Xe^{132}	57·54 ± ·17	57·79 ± ·21	57·58 ± ·20	57·48 ± ·15	56·54 ± ·24	57·39 ± ·31
Xe^{134}	81·54 ± ·27	82·04 ± ·24	81·66 ± ·14	81·54 ± ·15	81·54 ± ·27	81·54 ± ·23
Xe^{136}	100·00 ± ·24	100·00 ± ·24	100·00 ± ·20	100·00 ± ·17	100·00 ± ·27	100·00 ± ·32
Xe^{136} (%) from U^{238} S.F.	95·76	96·06	91·63	81·51	80·19	68·48

TABLE XII

FISSION-PRODUCT COMPONENTS AND THE Xe^{129} YIELD

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
U^{238} Spontaneous Fission (%)	95·86	96·15	91·82	81·65	80·42	68·65
U^{235} Neutron Fission (%)	4·14	3·85	8·18	15·19	17·22	25·23
U^{238} Neutron Fission (%)	0·00	0·00	0·00	3·16	2·36	6·12
$\frac{Xe^{129}}{Xe^{136}}$ x100 (Neutron Fission)	11·1	12·5	9·8	11·2	11·6	11·1

spontaneous fissions should be equal for the six determinations if no fission products have been lost. These ratios, expressed as percentages, are shown in Table XIII. It can be seen that these ratios are not equal, and hence that at least five of the minerals have incurred large losses of their fission product gases.

The absolute yield of Xe^{136} in U^{238} spontaneous fission has been estimated by Fleming and Thode(11) to be 6.5% and by Wetherill(12) to be 6.0%. The 6.30 ± .38% yield obtained from the Cinch Lake analysis is in agreement with these estimates and suggests that little or no fission product Xe^{136} has been lost from this mineral. Furthermore, it will be shown in the Discussion that the absolute xenon yields obtained from the Cinch Lake mineral are in good agreement with the corresponding iodine yields measured by Parker and Kuroda(13). It was therefore concluded that the Cinch Lake mineral could not have lost an appreciable portion of its fission product gases. The losses from the remaining five minerals are shown in the lower part of Table XIII.

TABLE XIII

THE RATIO OF Xe^{136} ATOMS FROM U^{238} SPONTANEOUS FISSION TO THE NUMBER OF FISSIONS

Mineral	Cinch Lake	Jahala Lake	Beaverlodge Lake	Great Bear Lake	Eagle Mine	Belgian Congo
Xe^{136} from U^{238} Spontaneous Fission (x 10^{14})	3·172 ± ·015	7·384 ± ·075	1·239 ± ·007	4·917 ± ·070	6·126 ± ·079	3·313 ± ·045
U^{238} Spontaneous Fissions (x 10^{16})	0·503 ± ·030	1·69 ± ·07	0·78 ± ·13	1·03 ± ·05	1·91 ± ·08	0·94 ± ·05
$\frac{Xe^{136} \text{ from S.F.}}{U^{238} \text{ S.Fissions}} \times 100$	6·30 ± ·38	4·38 ± ·18	1·59 ± ·26	4·78 ± ·23	3·21 ± ·13	3·51 ± ·17
Xe^{136} Loss (%)	0·0 ± 6·0	30·5 ± 6·6	74·8 ± 7·3	24·1 ± 7·1	49·0 ± 6·3	44·3 ± 6·5

DISCUSSION

U^{238} Neutron Fission in Uranium Minerals

The analysis summarized in Tables XI and XII indicates that measurable amounts of U^{238} neutron fission have occurred in three of the six uranium minerals. Since the neutron fission of U^{238} in nature has not been reported previously, it is necessary to determine if it is to be expected on the basis of laboratory fission experiments and whether the Xe^{131} abundances which were ascribed to U^{238} neutron fission could have been produced by other reactions.

U^{238} has a neutron fission cross section which is less than one barn in the Mev energy region and has a threshold at about 0.5 Mev. U^{235}, on the other hand, has a neutron-fission cross section which varies from about 1000 barns in the thermal energy range to about one barn in the Mev region. Since the present abundance of U^{238} in normal uranium is 99.27% and the mean energy of the neutrons emitted in fission is a few Mev, the presence of some U^{238} neutron fission is to be expected.

The ratio of U^{238} to U^{235} neutron fission in normal uranium is very sensitive to neutron energy and decreases by a factor of about 10^3 when the energy is reduced from 2 Mev to 0.5 Mev. Wanless and Thode(32) have shown that the fast neutron irradiation of normal uranium produces a fission ratio of about 1.5; whereas the irradiation with epithermal pile neutrons produces a ratio of about 0.16.

Tables II and XII show that there is a correlation between the concentration of uranium in a mineral and the percentage of neutron fission. Some gangue material, or country rock must of course be present in the crushed concentrate along with the uranium mineral. The inclusion of this extraneous material should be about the same for each of the six minerals since they were all separated to a density greater than three with di-iodo-methane. The percentage of uranium in the mineral concentrate should therefore approximate the uranium concentration in the mineral. The relation between the number of neutron-induced fissions and the uranium concentration in a uranium mineral is shown in Fig.7.

It had previously been assumed that the presence of the rare earths in uraninite was largely responsible for the low percentage of neutron fission in this mineral. The occurrence of U^{238} neutron fission in uranium minerals suggests much larger effective neutron energies than had been suspected, and indicates that the rare earths may have little effect on the amount of neutron-induced fission. The fact that the Jahala Lake uraninite and Cinch Lake pitchblende, with about equal uranium concentrations in the concentrates, show the same proportion of neutron-induced fission supports this conclusion.

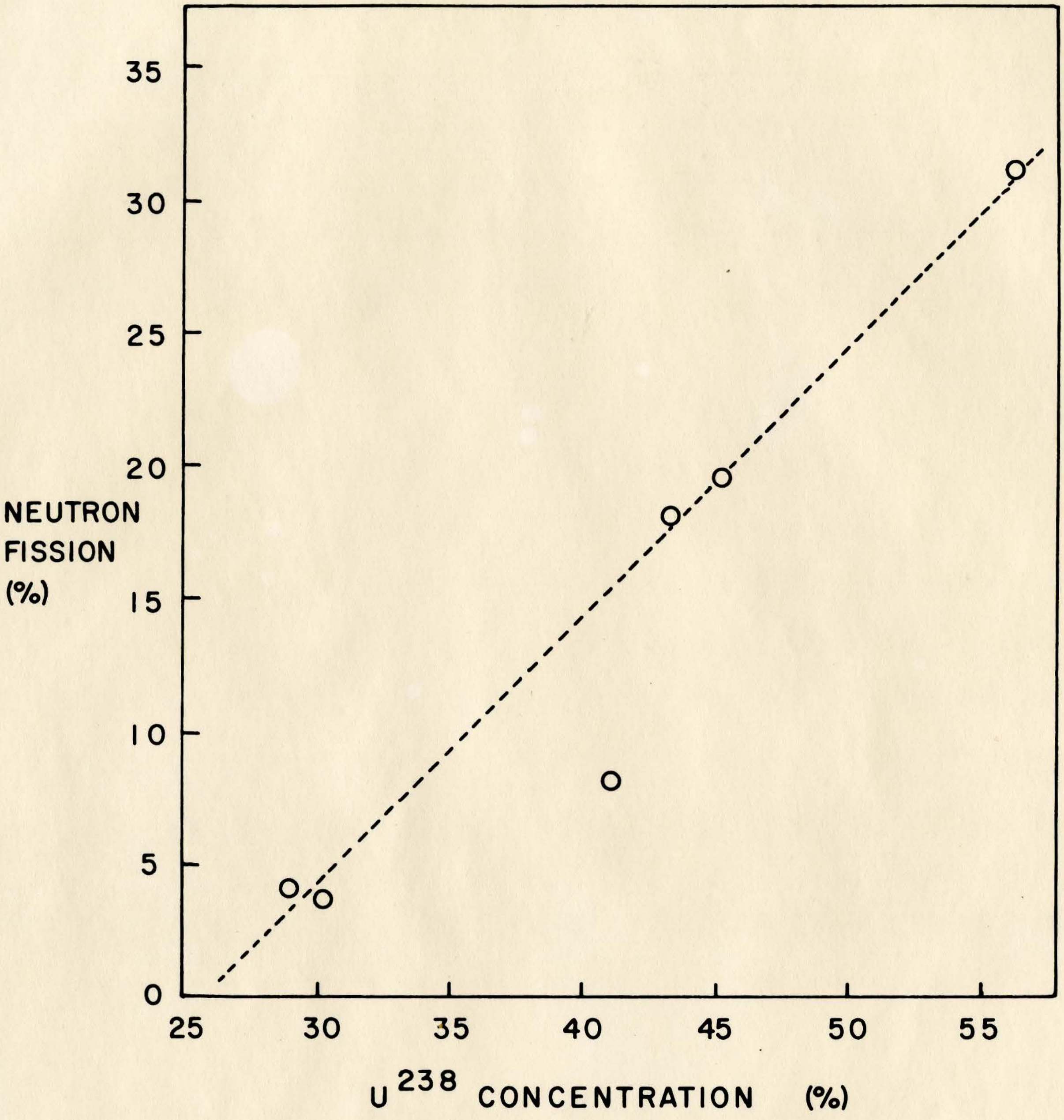

FIG. 7 RELATION BETWEEN THE AMOUNT OF NEUTRON FISSION AND URANIUM CONCENTRATION IN A URANIUM MINERAL OR ORE CONCENTRATE

Tables II and XII also suggest that the proportion of U^{238} neutron-induced fission in the neutron fission component decreases with decreasing uranium concentration in the concentrate. This correlation is not expected to be quantitative, however, because of the sensitivity of the ratio of of U^{238} neutron fission to U^{235} neutron fission to the effective neutron energy. A reduction in the effective neutron energy from 0.7 Mev to about 0.4 Mev would reduce this ratio from about 0.2 to a negligible level.

These observations indicate that the materials which dilute uranium in minerals are more effective as neutron absorbers than as neutron moderators. However, the decrease in neutron flux with increasing dilution of the uranium is accompanied by a small reduction in the effective neutron energy. This would result in a smaller proportion of the neutron-induced fission component from U^{238} fission. The low uranium content in the Jahala Lake and Beaverlodge Lake concentrates may therefore account for the lack of a U^{238} neutron fission component.

The Possibility of Xenon Contributions from the $Th^{232}(n,f)$ Reaction. Thorium is known to occur in very low abundance in pitchblende(37). This low concentration, together with the high threshold (1.2 Mev) for the $Th^{232}(n,f)$ reaction precludes measurable fission products from this source. Uraninite, on the other hand, may contain large quantities of thorium. The Jahala Lake uraninite, however, does not have a large enough effective neutron energy to produce a measurable U^{238} neutron fission component, and therefore must have a negligible amount of Th^{232} neutron fission.

The Possibility of Xenon Contributions from (n, γ) Reactions.

Neither the abundances nor the (n, γ) cross sections of the tellurium and barium contaminants in these uranium minerals are known. It is therefore not possible to predict the xenon yields from the three possible (n, γ) reactions. The increase in the corrected Xe^{131} abundances with the amount of neutron fission in the second analysis is, however, accompanied by an increase in the corrected Xe^{132} abundances. Since no (n, γ) reactions can feed the Xe^{132}, Xe^{134} or Xe^{136} abundances, and since the trends in both the Xe^{131} and Xe^{132} corrected abundances were removed by the introduction of a U^{238} neutron fission component in the third analysis, it may be concluded that contributions from (n, γ) reactions on tellurium and barium are negligibly small.

The Xe^{129} - I^{129} Discrepancy

In order to obtain internal consistency in the spontaneous fission patterns from the six mineral samples, using either the two component analysis, based on Xe^{134} and Xe^{136} or the three component analysis based on Xe^{131}, Xe^{134} and Xe^{136}, it was necessary to use a Xe^{129} yield in U^{235} fission which was 20% lower than the reported value. Purkayastha and Martin(36) first drew attention to this discrepancy in 1956 when they extracted the Xe^{129} and I^{129} from two uranium minerals and found that the I^{129} abundance was about 20% higher than would be expected from the Xe^{129} content. It is therefore necessary to consider those effects which might systematically lower the measured Xe^{129} fission product abundances in uranium minerals.

<u>Xe^{129} from U^{238} Neutron-induced Fission.</u> The presence of U^{238} neutron-induced fission in uranium minerals might be expected to affect the ratio of Xe^{129} to Xe^{136} in the neutron-induced fission component. The criterion for a satisfactory analysis of the fission-product patterns from the six minerals into their components, i.e. the equality of the corrected patterns, could be satisfied with other values of the ratio of the Xe^{129} relative yield in U^{235} neutron-induced fission to the yield in U^{238} neutron-induced fission than the one used. If, for example, the 129 mass chain yield in U^{235} thermal neutron fission reported by Purkayastha and Martin had been used, a satisfactory analysis would have required that the Xe^{129} yield from U^{238} neutron-induced fission be zero. The 129 chain yield in U^{238} neutron-induced fission has not been measured. It is possible, however, to interpolate with some confidence between the measured yields at Sb^{127} and Xe^{131} since the mass-yield curves for other fissile nuclei appear to be

unperturbed in this mass region. This interpolated Xe^{129} yield, expressed as a percentage of the Xe^{136} yield is 13.6 compared to 13.9 for U^{235} thermal neutron fission (Table VIII). There is at present no reason to believe that this yield should be appreciably lower than the interpolated value, and therefore the presence of some U^{238} neutron-induced fission in uranium minerals should not alter the ratio of Xe^{129} to Xe^{136} in the neutron fission components.

Primary Yields of I^{130} and the Normal Xenon Correction. It has been assumed that the measured Xe^{130} relative abundances from uranium minerals were due only to a normal xenon contamination. It is known, however, that I^{130}, which is shielded by stable Te^{130}, has a measurable primary yield in fission and decays to stable Xe^{130}.

The primary or independent yields of I^{130} from U^{235} and U^{238} fast neutron fission and from U^{238} spontaneous fission have not been measured. Kennett and Thode(17), however, measured these yields in U^{233} and U^{235} thermal neutron fission ($3.9 \times 10^{-3}\%$ and $5.0 \times 10^{-4}\%$ respectively) and showed that the neutron energy dependence of this yield in Pu^{239} fission was small. The fast neutron fission of U^{235} in uranium minerals should therefore produce an I^{130} primary yield of about $5.0 \times 10^{-4}\%$. The primary yields in U^{238} neutron fission and U^{238} spontaneous fission must be estimated from the systematics of primary yield formation.

The neutron enrichment of the uranium nucleus with increasing mass number should increase the displacement of the most probable charge of the fission fragments from the most stable charge, and hence reduce the I^{130} primary yield. Coryell, Brightsen and Pappas(38) have defined the most probable charge Zp for U^{235} neutron fission by:

$$Zp = Z_A - \tfrac{1}{2}\,(Z_A + Z_{(A^1 - A + 1)} - Z^1), \qquad (3)$$

where Z_A is the most stable charge for mass number A,
A^1 is the mass number of the fissioning nucleus,
Z^1 is the charge of the fissioning nucleus.

If it is assumed that the average number of neutrons from U^{238} neutron fission is about twice that from U^{233} or U^{235} neutron fission, it can be shown, using the Z_A values obtained by Grummit and Milton(39) and equation (3), that Z - Zp has an approximately linear increase with mass for the 130 mass chain in U^{233}, U^{235} and U^{238} neutron fission. The empirical charges distribution curve reported by Glendenin(7) and the 130 chain yields from the three kinds of fission can then be used to show that the primary yields of I^{130} in U^{235} and U^{238} neutron fission should be about one and two orders of magnitude less, respectively, than the corresponding yield in U^{233}. This prediction is confirmed for the yields from U^{233} and U^{235} neutron fission by the work of Kennett and Thode. The primary yield of I^{130} in U^{238} spontaneous fission should be less than that from U^{238} neutron fission since the 130 chain yield in the former is at least an order of magnitude smaller. Xe^{130} yields from U^{238} neutron fission and U^{238} spontaneous fission should therefore be small compared to this yield in U^{235} neutron fission.

The error introduced in the Xe^{129} fission product abundances in uranium minerals due to the neglect of the Xe^{130} contribution from U^{235} neutron fission is less than 1.2%, and hence cannot account for the Xe^{129} - I^{129} discrepancy.

Preferential Loss of Members of the 129 Mass Chain. The present work shows that uranium minerals may lose large portions of their fission-product inert gases. An isotopic fractionation accompanying this loss would result in a preferential loss of Xe^{129} relative to Xe^{136}. The maximum isotopic fractionation which could result from a diffusion loss would be 3%, however, and no mechanisms are known which could produce a 20% fractionation in xenon.

I^{129}, which was present to a few percent of the 129 mass chain during most of the mineral's history, could have been partially removed by leaching. The findings of Purkayastha and Martin, however, which suggest that I^{129} is high by about 20%, would require a continuous, large preferential loss of I^{129} which stopped a few million years ago.

The preceding discussion suggests that the I^{129} yield in U^{235} thermal neutron fission reported by Purkayastha and Martin may be about 20% high, since no reason could be found for a low Xe^{129} yield in uranium minerals.

Fractionation of Krypton Relative to Xenon

The Cinch Lake mineral, which seems to have lost none of its fission product gases, contains krypton fission products from U^{238} spontaneous fission which are about 20% higher than those from the other five minerals. This discrepancy can be attributed to the fractionation of krypton relative to xenon when fission product gases diffuse from a mineral. The absence of a quantitative correlation between fractionation and the apparent loss of fission products suggests that some of the minerals may have suffered a complete outgassing without a corresponding loss of radiogenic lead, or that some noble gases may have been lost by processes other than simple diffusion. In none of the five minerals other than Cinch Lake, however, could there have been a complete outgassing of the mineral followed by a complete retention of subsequent fission products.

The large losses of the inert gases from uranium minerals prevent the general use of accumulated xenon and krypton spontaneous fission products for age determination. Nevertheless, the fractionation accompanying loss should be a sensitive test of the validity of a 'fission product age', that is, the period during which fission products have accumulated without loss.

Comparison of the Xenon and Krypton Absolute Yields with other Absolute Yield Results.

Recently, Parker and Kuroda(13) and Ashizawa and Kuroda(14) have reported the absolute yields of Mo^{99} and several iodine isotopes from the spontaneous fission of U^{238}. These yields, along with the absolute yields of xenon and krypton from Cinch Lake pitchblende, are shown in Table XIV. The good agreement between the xenon and iodine yields at masses 131, 132 and 134 is in accord with the assumption that no fission product xenon and krypton had been lost from the Cinch Lake mineral. Segre's value of the U^{238} spontaneous fission half life has been used for all of the absolute yields obtained thus far, and hence does not enter into the comparison. The absolute yields from Table XIV are shown in the mass-yield curve of Fig.8.

The low yields at masses 133 and 135 have been ascribed by Ashizawa and Kuroda to large fine structure peaks at masses 132 and 134. Since no stable xenon isotopes exist at masses 133 and 135 and since a smooth curve can be drawn through the stable xenon fission product yields, it is not possible to confirm the existence of these fine structure effects from the present results.

TABLE XIV

ABSOLUTE YIELDS IN U^{238} SPONTANEOUS FISSION

	Absolute Yields (This Work)		Absolute Yields († Parker and Kuroda) (‡Ashizawa and Kuroda)	
Mass	Element	Yield (%)	Element	Yield (%)
83	Kr	0·0327 ± ·0028		
84	Kr	0·122 ± ·012		
85				
86	Kr	0·951 ± ·057		
99			Mo	6·4 ± ·5†
131	Xe	0·524 ± ·031	I	0·4 ± ·1‡
132	Xe	3·63 ± ·22	I	3·6 ± ·4‡
133			I	1·5 ± ·3‡
134	Xe	5·14 ± ·31	I	5·2 ± ·5‡
135			I	5·1 ± ·5‡
136	Xe	6·30 ± ·38		

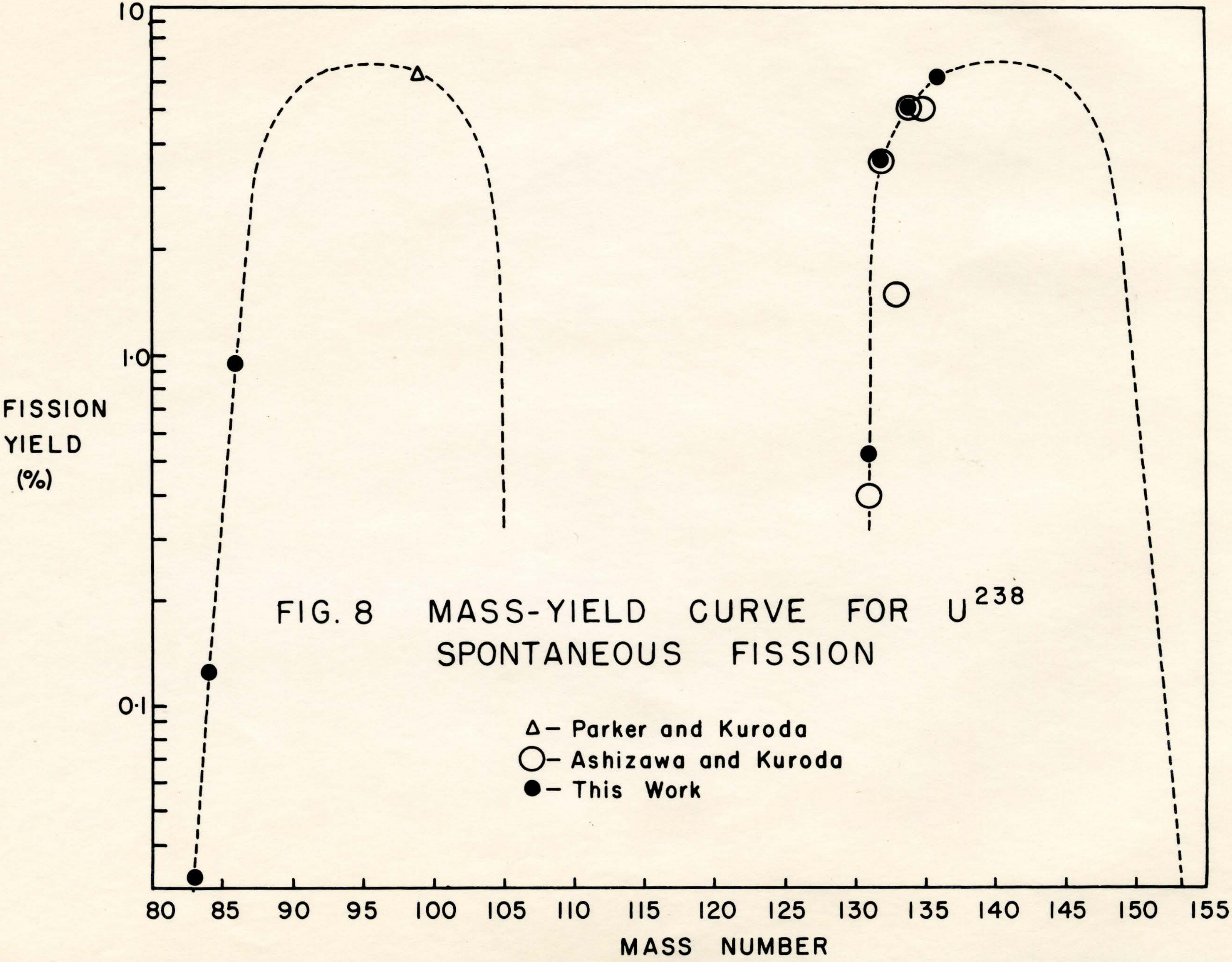

FIG. 8 MASS-YIELD CURVE FOR U^{238} SPONTANEOUS FISSION

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