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THE UTILIZATION OF HIGH SENSITIVITY NOBLE GAS MASS SPECTROMETRY IN THE DETECTION OF IODINE-129 AND PLUTONIUM-244

by

MERVET SALEH BOULOS
(The Former Mervet Maurice Saleh)
1945-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirement for the Degree

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

1972

T2636
82 pages
c.I

O K Manuel
Advisor

H. O. McDonald

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Bolter

226661

To My Husband

PUBLICATION THESIS OPTION

This dissertation consists of three manuscripts prepared for publication.

Pages 8-25 contain the manuscript published in Science **174**, 1334 (1971).

Pages 26-39 contain the manuscript published in Nature **235**, 150 (1972).

Pages 40-52 contain the manuscript submitted to Science.

ABSTRACT

Mass spectrometric analysis of the xenon isotopes in natural gas wells demonstrates that radioactive isotopes of element number 53 (I) and element number 94 (Pu) were present at the time of the Earth's formation. Evidence for the now extinct nuclide ^{129}I ($t_{1/2} = 17 \times 10^6$ years) was found in CO_2-rich gas while evidence for the now extinct ^{244}Pu ($t_{1/2} = 82 \times 10^6$ years) was discovered in other natural gas wells. The amounts of ^{129}I in thyroids was measured by combining neutron activation analysis with noble gas mass spectrometry. The current mammalian thyroid glands contain iodine with an isotopic composition $^{129}I{:}^{127}I \approx 1 \times 10^{-8}{:}1.0$.

ACKNOWLEDGMENTS

The author is deeply indebted to her advisor, Dr. Oliver K. Manuel, whose capability and direction were major factors in the accomplishment of this investigation. I also wish to acknowledge Dr. W. H. Webb for his guidance and help throughout my work, and Dr. H. O. McDonald for his helpful comments on the thesis manuscript.

My thanks go to my colleagues Dr. E. C. Alexander, Jr., Dr. B. Srinivasan, Dr. G. Zweerink, Mr. V. J. Becker, Mr. R. D. Beaty and Mr. D. E. Sinclair for their assistance, with special thanks to Mr. E. W. Hennecke for his help in the laboratory and instruction in the techniques of glass blowing. I also wish to thank Mr. Leo Fanger for his cooperation and Ms P. Johnson for typing this dissertation.

My deepest gratitude goes to my parents for their unfailing encouragement, which has been a great incentive throughout my years of study. An equally deep gratitude goes to my husband for his constant encouragement, help and patience which have made it possible for me to pursue my education.

The research described in this dissertation was supported by grants from the National Science Foundation.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Page

II. THE XENON RECORD OF EXTINCT RADIOACTIVITIES IN THE EARTH

III. EXTINCT RADIOACTIVE NUCLIDES AND PRODUCTION OF XENON ISOTOPES IN NATURAL GAS

V. APPENDICES

A. Preparation of Natural Gas Samples for Mass Spectrometric Analysis

C. Mass Spectrometric Analysis

LIST OF TABLES

Page

II. THE XENON RECORD OF EXTINCT RADIOACTIVITIES IN THE EARTH

III. EXTINCT RADIOACTIVE NUCLIDES AND PRODUCTION OF XENON ISOTOPES IN NATURAL GAS

IV. IODINE-129 IN THYROID GLANDS

INTRODUCTION

This dissertation primarily deals with the use of a mass spectrometer, especially designed for the study of noble gases, as a highly sensitive analytical tool. The work described in the first two papers was undertaken in order to search for the decay products of two now-extinct radioactive nuclei in the earth, while the work presented in the third paper was undertaken in order to determine the present levels of radioactive ^{129}I in contemporary biological systems. Both efforts were successful.

For purposes of introduction, a brief review of literature pertinent to the manuscripts contained in Sections II and III of this dissertation will be presented first, followed by a review of literature related to the manuscript contained in Section IV.

The age of our solar system and the planet Earth has long been a subject of interest, speculation and research. According to presently accepted theories of solar evolution, all planets of the solar system condensed from the primordial solar nebula at approximately the same time. The terrestrial and meteoritic occurrence of radioactive nuclides such as ^{232}Th, ^{238}U, ^{40}K, and ^{235}U with half-lives of 1.4×10^{10}, 4.5×10^{9}, 1.3×10^{9}, and 7.1×10^{8} years, respectively, are an indication that conditions as we know them today cannot have existed in the solar system for a time very long compared to these half-lives.

Our 'sampling' of the solar system is very limited. We have only limited access to the Earth's crust, little or no reliable sampling of material below the crust, and a random sampling of meteorites and lunar surface material. Several radioactive dating methods place the time of formation of most meteorites at 4.6×10^9 years ago, while the rocks and minerals from the surfaces of the Earth and Moon show a wide range of ages with an upper limit of about 4×10^9 years. However, a comparison of the isotopic composition of terrestrial lead from oceanic sediments[1] with that of lead from stone and iron meteorites suggests that the Earth and the meteorites may have formed at approximately the same time, 4.6×10^9 years ago.

Uranium-235, with a half-life of 7.1×10^8 years, is the shortest-lived primordial nuclide which occurs naturally in measurable quantities. All shorter-lived primordial nuclides, which may have existed in the early solar system, would now be extinct. It has been established that two extinct radioactivities, ^{129}I and ^{244}Pu, were incorporated in meteorites at the time of their formation[2]. They were both identified from their stable xenon decay products. The ^{129}I decays with a half-life of 17 million years to ^{129}Xe, while ^{244}Pu with a half-life of 82 million years gives rise to the heavy xenon isotopes $^{131-136}$Xe by spontaneous fission.

Reliable evidence for the past existence of either of these extinct

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activities had not been previously reported in any terrestrial material. Samples of natural gas appeared promising in the search for extinct radioactivities, since previous investigations of their noble gas content had revealed large excesses of radiogenic ^{4}He and ^{40}Ar, together with a xenon isotopic composition different from atmospheric xenon in ways that were not fully understood. Thus most gases showed enrichments of the heavy isotopes, ^{131}Xe to ^{136}Xe, with yields at ^{131}Xe and ^{132}Xe unlike those expected from the spontaneous fission of ^{238}U. Several investigations also showed what appeared to be a small enrichment of the ^{129}Xe isotope.

We therefore undertook a reinvestigation of the isotopic composition of xenon in natural gas. By taking great precautions to prevent atmospheric contamination, which might dilute isotopic anomalies and render them undetectable, we have discovered conclusive evidence for the past existance of ^{129}I as well as a clear indication for the past existance of ^{244}Pu in the Earth's early history.

In the manuscript presented in Section II of this dissertation, natural gas from a 99.9% CO_2-rich well was selected for study. Gases in such pools may have resulted from volcanic emanation or from the decomposition of carbonate rocks through contact with intrusive magmas[3]. Mass spectrometric analysis of this gas revealed a 10%

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[3] W. A. Butler, P. M. Jeffery, J. H. Reynolds, G. J. Wasserburg, J. Geophys. Res. 68, 3283 (1963).

enrichment of ^{129}Xe and enrichments in the heavy isotopes $^{131-136}$Xe with a 12% enrichment of the ^{136}Xe over its atmospheric abundance. The observed enrichment in ^{129}Xe far exceeds that expected from any known nuclear reactions that are presently taking place in nature. We therefore conclude that this is the decay product of part of the Earth's original inventory of ^{129}I. The presence of radiogenic ^{129}Xe in CO_2 wells shows that any quantitative degassing of the Earth must have been limited to a relatively short time period, or more likely, that the degassing process was never quantitative but has decreased over geologic time. Further, the amounts of radiogenic ^{129}Xe in the CO_2 wells demonstrate that the earth started to accumulate this decay product no later than some meteorites. These results therefore place narrow limits on any age difference between the Earth and the oldest meteorites.

In the manuscript presented in Section III of this dissertation the isotopic composition of xenon in four additional natural gas samples is presented. It is shown that small effects from isotopic mass dependent fractionation are superimposed on the xenon isotope spectra in well gases. On correcting for this, the remaining xenon shows a small excess of ^{129}Xe in all well gas samples and a consistent pattern for the enrichment of heavy xenon isotopes. This enrichment pattern cannot be accounted for by the fission products of ^{238}U alone, but it is shown that the enrichment of heavy xenon isotopes in these gas samples results from a mixture of fission products from ^{238}U and ^{244}Pu. Thus, the results presented in Section II and Section III of this dissertation demonstrate unambiguously that ^{129}I and ^{244}Pu were present in the elements that originally formed the Earth.

In the manuscript presented in Section IV of this dissertation, the present levels of $^{129}I/^{127}I$ were determined in human, sheep and cattle thyroid glands. The primordial abundance of ^{129}I has decayed to $\approx 10^{-80}$ of its original inventory over the 4.5×10^9 year history of the Earth. However, ^{129}I is being continuously produced on the Earth's surface by spallation reactions on xenon in the upper atmosphere, by spontaneous fission, by neutron capture reactions in tellurium, and recently by nuclear reactors and weapons. Attempts at direct measurement of the ^{129}I level in nature are hampered by the very low activity of this nuclide. Indirect measurements of the ^{129}I in samples of natural iodyrite[4] have shown that, prior to the nuclear age, $2.2 \times 10^{-15} \leq {}^{129}I/^{127}I \leq 3.3 \times 10^{-15}$. However, attempts to measure this same ratio, by means of neutron activation analysis followed by detection of the radioactivity of ^{130}I and ^{128}I, has yielded tentative values[5] which are about five orders of magnitude higher.

It is of considerable importance to determine the present

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amount of iodine-129 in biological cycles. Only a few attempts have been made at this determination[6, 7] using neutron activation analysis coupled with γ-ray spectrometry. However, the ratios obtained seemed suspect in view of the large discrepancy between the results obtained for iodyrite by this and the mass spectrometric measurements.

Since iodine accumulates in the thyroid glands of animals, samples of iodine extracted from the thyroid glands of humans, sheep and cattle were used in our study of ^{129}I in animals. The procedure involved neutron activation analysis followed by high sensitivity noble gas mass spectrometry as described in Section IV and Appendix B of this dissertation. This combination of analytical methods proved to be extremely sensitive. Current mammalian thyroid iodine was found to have an isotopic composition of $^{129}I/^{127}I \approx 1 \times 10^{-8}$.

The intrinsic characteristics of iodine-129 make it an ideal tracer[8]. Its long half-life makes it possible to store ^{129}I-labeled

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compounds for long periods of time and permits the use of ^{129}I as a tracer in very slow processes. For use as a tracer in biological systems, the extremely low specific activity of ^{129}I greatly reduces the radiation effects associated with the more commonly used ^{131}I. Development of a highly sensitive method for detecting ^{129}I, as described in Section IV of this dissertation, permits ready access to the many advantages of ^{129}I as a clinical, biological and geological tracer.

II. THE XENON RECORD OF EXTINCT RADIOACTIVITIES IN THE EARTH

Manuscript as published in Science, **174**, 1334 (1971).

Abstract. Analyses of xenon from well gas rich in carbon dioxide reveal a large excess of radiogenic xenon-129 from the decay of extinct iodine-129. Smaller excesses observed in the heavy xenon isotopes are from fission. These results place narrow limits on any age difference between the earth and the oldest meteorites. The occurrence of excess radiogenic xenon-129 in well gas also suggests that any quantitative degassing of existing solid materials to form the atmosphere must have been limited to a very early period of the earth's history, approximately the first 10^8 years. Alternately this observation is consistent with a model of the earth's continuous, but still incomplete, degassing since its time of formation.

There is unambiguous evidence from several radioactive dating methods that most meteorites formed about 4.6 x 10^9 years ago (1, 2). This age is obtained by comparing present concentrations of certain long-lived radioactive nuclides, ^{238}U, ^{235}U, ^{87}Rb, and ^{40}K, with the concentrations of their respective stable decay products, ^{206}Pb, ^{207}Pb, ^{87}Sr, and ^{40}Ar. It has recently been established that two radioactive nuclides, ^{129}I and ^{244}Pu, were incorporated into meteorites at the time of their formation (3), but essentially the entire inventory of these two nuclides has decayed over the life-span of 4.6 x 10^9 years of meteorites. These two nuclides are now referred to as extinct radioactivities.

The half-lives of ^{129}I and ^{244}Pu are 17 x 10^6 (4) and 82 x 10^6 (5) years, respectively, and their decay products identified in meteorites are radiogenic ^{129}Xe (^{129r}Xe) from ^{129}I and fissiogenic $^{131\text{-}136}Xe$ ($^{131\text{-}136f}Xe$) from ^{244}Pu. Because it is not possible to calculate the age of a body solely from the concentration of a stable decay product, total meteorite ages cannot be obtained by either ^{129}I-^{129r}Xe or ^{244}Pu-$^{131\text{-}136f}Xe$ dating. However, early $^{129}I:^{127}I$ and $^{244}Pu:^{238}U$ ratios in meteorites decreased rapidly because of the shorter half-lives of the nuclides in the numerator, and since the nuclides in each ratio display similar geochemical behavior, measurements of the $^{129r}Xe:^{127}I$ and $^{131\text{-}136f}Xe:^{238}U$ ratios present in meteorites today are used to define the $^{129}I:^{127}I$ and $^{244}Pu:^{238}U$ ratios present when the meteorites formed (6, 7). For example, it has been found that chondrite meteorites were formed when the $^{129}I:^{127}I$ ratio was about 1.1 x 10^{-4}

(8) and the ^{244}Pu : ^{238}U ratio was about 0.013 (7). In several different achondrites the initial ^{129}I : ^{127}I ratio was found to vary from 10^{-8} to 10^{-5}, and the initial ^{244}Pu : ^{238}U ratio varied from 0.002 to 0.006 (9), which suggests that the achondrites formed later than the chondrites. Meteorite age differences of a few million years have been detected by measurements of ^{129r}Xe : ^{127}I and $^{131-136f}$Xe : ^{238}U ratios (9, 10).

The chronology of early events for the earth is not so well established. The earth's interior is inaccessible, and the rocks and minerals of the earth's crust show a wide range of ages with an upper limit of about 3.5 x 10^9 years. Further, the continuous formation of new crustal material along oceanic ridges suggests that even today the earth's crust is not completely isolated from its mantle. Thus, the fundamental assumption of all radioactive dating, that the system has remained isolated or closed over the time period being measured, may not be valid for the accessible portions of the earth. Age estimates of the earth based on ^{207}Pb : ^{206}Pb ratios are undoubtedly among the more reliable since chemical fractionation would alter neither the ratio of the two parents, ^{235}U : ^{238}U, nor the ratio of the decay products, ^{207}Pb : ^{206}Pb. The ^{207}Pb : ^{206}Pb ratios in oceanic sediments, lead ores, and old shield-area rocks suggest that the earth is approximately the same age as meteorites (2, 11). Even so, no clear evidence has previously been presented for the occurrence on earth of the decay products of the extinct radioactivities, ^{129}I or ^{244}Pu.

The search for decay products of extinct elements in the earth has included several studies of xenon from gas wells (12-15). Boulos and Manuel (14) suggested that the xenon from deep gas wells up to a depth of 54.9 km was enriched in the heavy isotopes because of isotopic fractionation but noted that ^{129}Xe seemed to be enriched because of the decay of ^{129}I within the earth. Butler et al. (15) reported a small component of excess ^{129}Xe and an enrichment of the heavy xenon isotopes in CO_2 well gas from Harding County, New Mexico. They noted that the ^{129}Xe anomaly, if real, was due to the decay product of ^{129}I. In view of the uncertainty in the identification of the decay product of ^{129}I in terrestrial gas samples, a reinvestigation of CO_2 well gas from Harding County was undertaken. The samples were taken from a well drilled in 1969 in a field known as the Bueyeros Pool. The well has a depth of 6432 m and a wellhead pressure of 480 pounds per square inch (3312 N/m^2). Methods of gas analysis and data reduction were described by Bennett and Manuel (12). The results of mass spectrometric analyses on duplicate samples are shown in Table 1 together with the isotopic composition of atmospheric xenon (16). The xenon concentration per unit volume of gas is about 1/10,000 of that in air.

Within the limits of statistical error, the isotope ratios from these two analyses are identical and correspond to atmospheric xenon at all mass numbers except 129, 132, 134, and 136. The abundance pattern of the xenon isotopes relative to that in the atmosphere (16) does not fit the pattern expected from isotopic fractionation (17). The ^{129}Xe

isotope is enriched by about 10 percent over its atmospheric abundance, and the ^{136}Xe isotope is enriched by about 12 percent. The amount of excess ^{129}Xe we attribute to the decay of now extinct ^{129}I and show this as ^{129r}Xe near the bottom of Table 1. In a similar manner the amount of excess ^{136}Xe we attribute to fission decay and designate this as ^{136f}Xe. We are certain that both of these anomalies are real and that terrestrial xenon therefore contains a record of extinct elements that were present in the very early history of the earth.

The presence of ^{129r}Xe in the CO_2 well gas is evidence that part of the xenon was derived from material that has not mixed with atmospheric xenon since a very early period when the earth's original inventory of ^{129}I had not completely decayed. The CO_2 may have resulted from volcanic emanations or from decomposition of carbonate rock through contact with intrusive magmas (15). Thus, the well may contain a mixture of gases from magmas and carbonates. The great majority of the New Mexico pools rich in CO_2 gas lie close to regions of recent igneous activity (18), and it seems likely that the very old xenon component, indicated by radiogenic ^{129}Xe, came from magmas, while the bulk of the CO_2, and probably other constituents, were derived from crustal carbonates.

Enrichments due to radiogenic and fissiogenic xenon were calculated by subtracting atmospheric xenon (16) from the average xenon observed in the two samples of CO_2 well gas,

$$\delta_i = (^{i}Xe : {}^{130}Xe)_{CO_2\ well} - (^{i}Xe : {}^{130}Xe)_{air} \qquad (1)$$

where i is the mass number and ^{130}Xe is the reference isotope because it is shielded from any contribution from fission. The results are shown in Fig. 1 with the yields of xenon isotopes from the spontaneous fission of ^{238}U (19) and ^{244}Pu (20).

The large excess of ^{129}Xe relative to excess $^{131-136}$Xe is unlike any known fission yields (21). Butler et al. (15) have considered alternative possible origins for excess ^{129}Xe in CO_2 gas and concluded that the decay of now extinct ^{129}I is the most likely source. Srinivasan et al. (22) have shown that natural iodine, as incorporated in the mineral iodyrite (AgI), contained a small amount of ^{129}I from nuclear reactions in nature. They showed that nuclear reactions in the earth yielded a maximum equilibrium ratio for the two iodine isotopes of $^{129}:^{127}\mathrm{I} \leq 3.3 \times 10^{-15}$. This ratio and the average iodine content of limestone, 14 parts per million (23), can be used to show that only about 4×10^{-20} cm^3 of excess ^{129}Xe per 1 cm^3 of CO_2 gas could be derived from the decomposition of crustal carbonate rocks. This is almost seven orders of magnitude less than the amount of excess ^{129}Xe observed in our analyses. Since neither the present levels of ^{129}I (22) nor any known nuclear reactions in nature (15) are capable of producing the excess ^{129}Xe shown in Fig. 1, we conclude that this is the decay product of part of the earth's original inventory of ^{129}I.

From our measurements, it is not possible to unambiguously determine the origin of the fission products, $^{131-136f}$Xe. As can be seen from Fig. 1, the average yields at ^{131}Xe, ^{132}Xe, and ^{134}Xe relative to the yield of ^{136}Xe are slightly higher than the yields reported for the spontaneous fission of ^{238}U (19). Butler et al. (15) also reported high yields of ^{131}Xe and ^{132}Xe in CO_2 gas but ruled out any appreciable contribution from neutron-induced fission of ^{235}U by the high ^{134}Xe : ^{136}Xe ratio in the latter. A mixture of fission products from ^{244}Pu and ^{238}U, about 31 percent of the excess ^{136}Xe from ^{244}Pu and about 69 percent of the excess ^{136}Xe from ^{238}U, fits the average yields from our two analyses. However, within the statistical error of our measurements the total enrichment of heavy xenon isotopes, $^{131\text{-}136}$Xe, could be from either ^{238}U (19) or ^{244}Pu (20). Even in the absence of definite information on the origin of $^{131\text{-}136f}$Xe, the data from Table 1 place narrow limits on the age of the earth relative to that of meteorites.

It is impossible to make a quantitative calculation of the formation time of the earth from the concentration of ^{129r}Xe in the CO_2 wells without information on the iodine content and the quantity of magma that released this decay product. However, even if all the observed ^{136f}Xe in the CO_2 well is from ^{244}Pu and if both ^{129r}Xe and ^{136f}Xe were derived exclusively from magma with the highest iodine: uranium ratio observed in deep-seated rocks (24), it can be shown by the method of Sabu and Kuroda (9) that the earth formed and began to accumulate radiogenic ^{129r}Xe no later than the achondrites. This means that any period of complete degassing, as might have accompanied the differentiation of the earth into a core, mantle, crust, and atmosphere, must have been limited to approximately the first 10^8 years of the earth's history. It should be emphasized that this age estimate is based on an assumption that all of the ^{136f}Xe in the CO_2 wells is from ^{244}Pu. If part of the ^{136f}Xe is from uranium or if part of the decay products were derived from material with a lower iodine: uranium ratio than assumed above, then an even earlier time of retention of these decay products in the earth is indicated.

The occurrence of ^{129r}Xe in well gas suggests the possibility of radiogenic ^{129}Xe in the terrestrial atmosphere. A comparison (Fig. 2) of atmospheric xenon (16) with xenon implanted in lunar soil (25) from the solar wind shows that these two types of xenon are related by isotopic fractionation (17) except for a clear excess of ^{129r}Xe in air and an apparent excess of ^{136f}Xe in the moon. The fractional abundance of ^{124}Xe and ^{126}Xe in natural xenon is only about 10^{-3}, and deviations from the fractionation line for these two isotopes are probably the result of nuclear reactions (26).

In conclusion, the presence of radiogenic ^{129}Xe in CO_2 wells shows that the earth started to accumulate this decay product no later than did some achondrites. Any quantitative degassing of the earth must have been limited to a relative short time period. It seems more likely to us that the degassing process was never quantitative but has decreased over geologic time as suggested by Turekian (27). The presence of ^{129r}Xe in the atmosphere with no clear evidence of ^{136f}Xe suggests that the initial retention of these decay products in terrestrial material may predate the formation of achondrites. The decay products of extinct elements in the earth are excellent tracers for studies of the events in the early history of the earth (28).

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28. This investigation was supported by the National Science Foundation, NSF-GA-16618. We are deeply indebted to Mr. J. T. Crow and Mr. August Hayoz of the SEC Corporation for their cooperation and generosity in providing these excellent samples of CO_2 gas. Our special thanks go to Mr. E. W. Hennecke and Mr. B. Srinivasan for assistance in the laboratory and for many valuable comments. Comments by Mr. J. W. Koenig were helpful in revising the manuscript.

TABLE 1. XENON IN CO_2 WELL GAS AND IN AIR

Xenon Isotopes	Relative Abundance of isotopes Sample 1 126 cc STP	 Sample 2 78 cc STP	 Air (16)
^{124}Xe	2.35 ± 0.10	2.41 ± 0.06	2.35
^{126}Xe	2.25 ± 0.10	2.30 ± 0.06	2.21
^{128}Xe	46.9 ± 0.5	47.5 ± 0.5	47.0
^{129}Xe	711 ± 6	707 ± 4	648
^{130}Xe	≡100	≡100	≡100
^{131}Xe	521 ± 5	524 ± 3	519
^{132}Xe	677 ± 6	676 ± 5	659
^{134}Xe	278 ± 2	279 ± 3	256
^{136}Xe	241 ± 2	245 ± 3	217
Gas Concentrations ($\times 10^{-15}$ cm^3/cm^3 gas STP)			
Total ^{130}Xe	300 ± 60	400 ± 80	3,550,000
^{129r}Xe	189	236	----
^{136f}Xe	72	112	----

Fig. 1. The excess xenon isotopes found in CO_2 gas wells relative to atmospheric xenon (16). The excess for each isotope of mass number i is expressed as $\underline{\delta_i}$, which is defined by Eq. 1 (see text). The enrichment at each mass number is compared with that expected from the fission of ^{244}Pu (20) and ^{238}U (19).

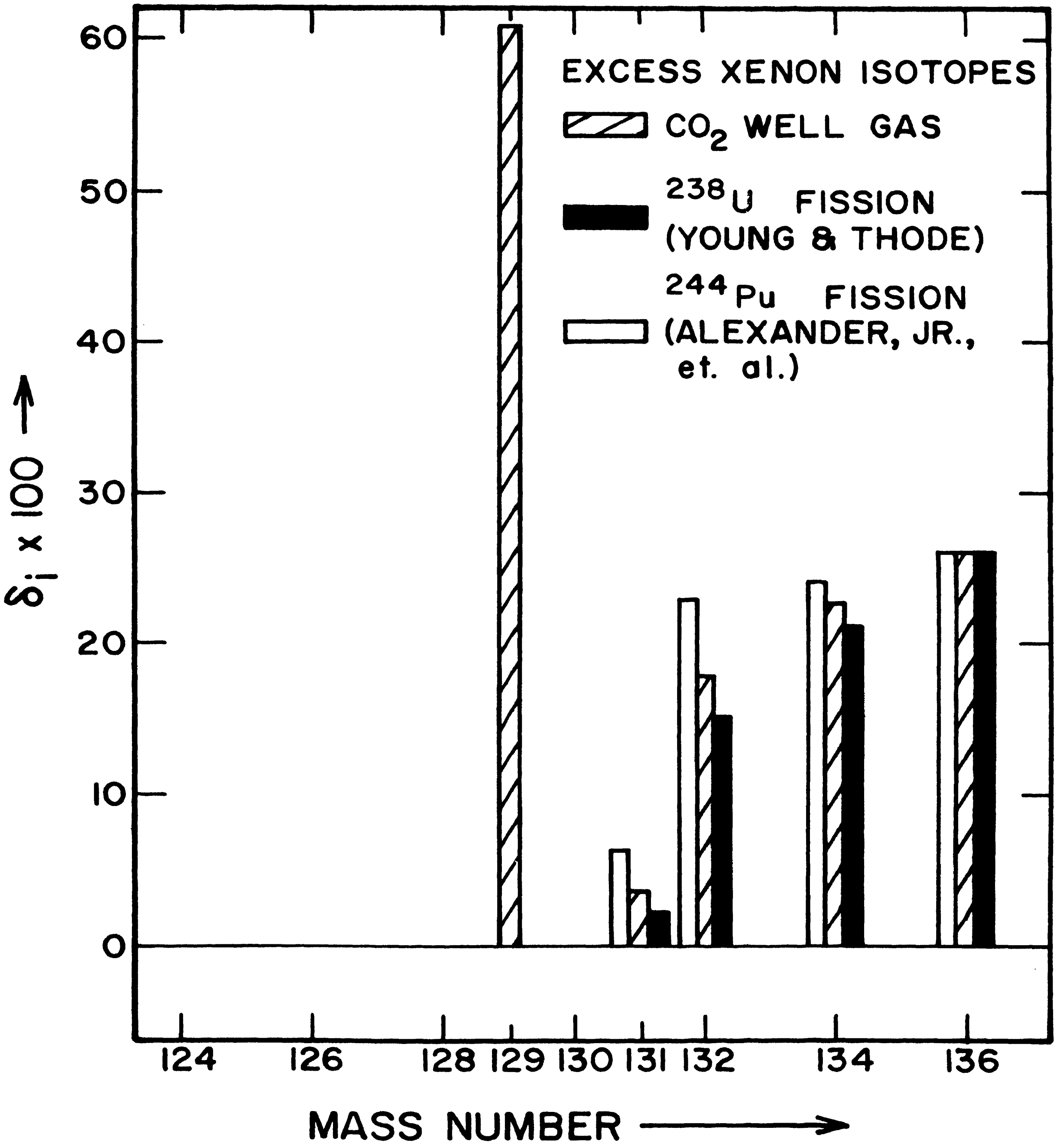
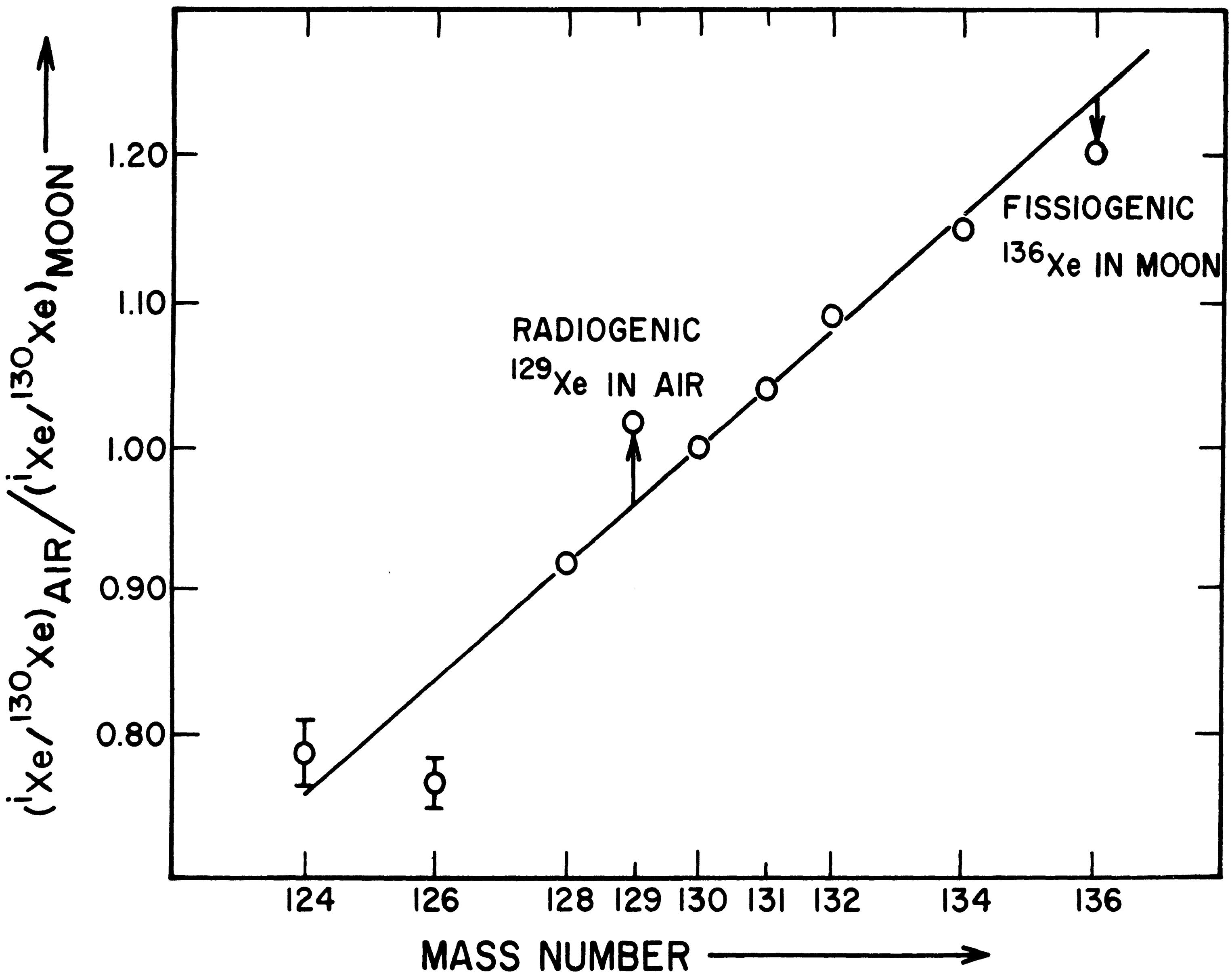

EXCESS XENON ISOTOPES
CO$_2$ WELL GAS
^{238}U FISSION (YOUNG & THODE)
^{244}Pu FISSION (ALEXANDER, JR., et. al.)
$\delta_i \times 100$
0
10
20
30
40
50
60
124
126
128
129
130
131
132
134
136
MASS NUMBER

Fig. 1

Fig. 2. The ratio of xenon in air (16) to xenon released from lunar soil at 800°C (25). The line shows the effects of isotopic fractionation. Deviations from isotopic fractionation at ^{129}Xe and ^{136}Xe are due to radiogenic ^{129}Xe in air and fissiogenic ^{136}Xe in the moon, respectively.



$({}^{i}Xe/{}^{130}Xe)_{AIR}/({}^{i}Xe/{}^{130}Xe)_{MOON}$
1.20
1.10
1.00
0.90
0.80
RADIOGENIC
${}^{129}Xe$ IN AIR
FISSIOGENIC
${}^{136}Xe$ IN MOON
124
126
128
129
130
131
132
134
136
MASS NUMBER

Fig. 2

III. EXTINCT RADIOACTIVE NUCLIDES AND PRODUCTION OF XENON ISOTOPES IN NATURAL GAS

Manuscript as published in Nature Physical Science, **235**,
150-152 (1972).

It has been established from isotope studies of xenon in meteorites that two radioactive nuclides that are now extinct once existed in the solar system. In 1960 Reynolds[1] discovered radiogenic ^{129}Xe, the decay product of ^{129}I, in the Richardton chondrite, and in 1965 Rowe and Kuroda[2] found an enrichment in the heavy xenon isotopes $^{131-136}Xe$ in the Pasamonte achondrite due to the spontaneous fission of ^{244}Pu. Terrestrial lead from oceanic sediments fits the isochron defined by the lead isotopes in meteorites[3], which suggests that the Earth also formed at a time when ^{129}I and ^{244}Pu were present among the elements of the solar system.

The occurrence of radiogenic ^{4}He and ^{40}Ar in natural gas wells prompted several studies of xenon in these gases. All reports[4-7] showed an enrichment in the heavy xenon isotopes $^{131-136}Xe$, but the enrichment observed for ^{131}Xe and ^{132}Xe in three of the analyses[4,5,7] was greater than that expected from the spontaneous fission of ^{238}U. Small enrichments in ^{129}Xe were also observed[4,6,7] in some of the well gases. Clear evidence has recently been reported[8] for the decay product of ^{129}I in natural gas that is rich in CO_2; the ^{129}Xe isotope was enriched by $\approx 10\%$ relative to its abundance in atmospheric[9] xenon. These gases also displayed a prominent enrichment of the heavier isotopes $^{131-136}Xe$, and the yields were intermediate between the spontaneous fission yields[10] of ^{238}U and the spontaneous fission yields[11] of ^{244}Pu. Within the experimental error limits of the measurement, however, spontaneous fission of either ^{238}U or ^{244}Pu could account for all the excess $^{131-136}Xe$ in gas that is rich in CO_2 (ref. 8).

To obtain reliable isotopic data with which to examine plausible mechanisms for the production of xenon isotopic patterns in other natural gases, we analysed large volumes (2 to 4 cm^3 STP) of gas from four deep wells. Data on the source, the volume analysed and the principal constituents of these gases are given in Table 1. No previous report on the xenon content of three of these samples has been given, but sample G-1 is from the same plant as one of the samples, C-16, analysed by Bennett and Manuel[7]. Sample G-1 was, however, collected from the Lisbon plant about three years later than sample C-16, and as the plant contains a mixture of gases from seventeen different wells, there is no assurance that these two samples represent the same gas. Great care was taken in sampling and analysing these gases to prevent atmospheric contamination or any possible fractionation. Details of the sampling procedures, the mass spectrometric analysis and the method of data reduction are given elsewhere[7-12].

Table 2 shows the isotopic composition of xenon for the four natural gas samples analysed, together with the isotopic composition of xenon in air[9] and in other gas wells[5, 8]. The xenon in all the wells shown in Table 2 contains an enrichment in ^{129}Xe. The xenon in G-1, Navajo and the two samples of gas rich in CO_2 shows a clear excess of the heavier xenon isotopes. The enrichment of each xenon isotope of atomic mass number <u>m</u> due to its production by nuclear processes is

$$^{m}\delta = [(^{m}Xe/^{130}Xe)_{Gas} - (^{m}Xe/^{130}Xe)_{Trapped} \qquad (1)$$

We have chosen ^{130}Xe as the reference isotope in equation (1) for the reasons given by Kuroda[13]. The abundance of this nuclide is fairly large; it is shielded by ^{130}Te, the amount of ^{130}Xe produced by fission is negligible, and there is very little possibility for the production of ^{130}Xe by other nuclear reactions.

To obtain reliable information on the xenon component arising from nuclear decay, it is essential to identify isotopic anomalies resulting from fractionation effects in the trapped xenon component. The role of mass dependent fractionation in generating isotopic anomalies of noble gases in the Earth and in meteorites has been noted by several investigators[14-20]. Further, Boulos and Manuel[21] noted that large enrichments of heavy xenon isotopes in some natural gas samples correlated with high ^{38}Ar/^{36}Ar ratios as well as with large enrichments of xenon relative to the lighter noble gases. The isotopic ratios shown in Table 3 are from natural gas wells analysed by Bennett and Manuel[7] and illustrate isotopic correlations suggestive of mass dependent fractionation.

From Table 2 we note that the ratios ^{124}Xe/^{130}Xe, ^{126}Xe/^{130}Xe and ^{128}Xe/^{130}Xe in G-1 and in the two CO_2 rich gas samples are generally higher than these ratios in atmospheric xenon, whereas the Navajo gas shows slightly lower ratios. By a comparison of the abundance pattern of these nonradiogenic xenon isotopes in the gas samples with their abundance in atmospheric xenon, we estimate that the trapped xenon in G-1, Navajo, CO_2-gas I and the CO_2-gas II is depleted in the heavy isotopes, as a result of mass fractionation, by factors of +0.34%, -0.23%, +0.12% and +0.66% per mass unit, respectively. Assuming that the trapped xenon in each gas is atmospheric xenon which has been subjected to the above fractionation, we employ equation (1) to calculate the contribution $^{m}\delta$ from nuclear decay at m = 129, 131, 132, 134, and 136.

Fig. 1 compares the ratios $^{m}\delta/^{136}\delta$ for these three natural gases with the spontaneous fission yields of ^{238}U and ^{244}Pu as reported by Young and Thode[10] and Alexander et al.[11], respectively. The error limits shown in Fig. 1 were calculated from the statistical errors reported on the isotope ratios of xenon in each natural gas. No fission yield is shown for ^{129}Xe as the spontaneous fission of ^{238}U yields[22] $^{129}\delta/^{136}\delta \leq 0.002$, and the yield of ^{129}Xe from the spontaneous fission of ^{244}Pu has not been measured.

The xenon from all four natural gas wells shown in Fig. 1 displayes an enrichment of the heavy xenon isotopes which seems to be between the fission yields of ^{238}U and ^{244}Pu. The fission yields for ^{131}Xe and/or ^{132}Xe in G-1, CO_2-gas II, and in the Navajo gas cannot be accounted for by simple spontaneous fission of ^{238}U. Clark and Thode[5] suggested that the discrepancies between the fission yields of ^{131}Xe and ^{132}Xe from ^{238}U and the large excess of ^{131}Xe and ^{132}Xe observed in the Navajo gas could be due to preferential leakage of these two fission products from materials rich in uranium. Their hypothesis cannot be excluded and may account for many variations observed in the fission yields of xenon in nature, as this mechanism might result in abnormally high yields of ^{131}Xe and ^{132}Xe in the gas which escapes, and in abnormally low yields of ^{131}Xe and ^{132}Xe in the gas which accumulates in ores that are rich in uranium.

But because all the gas samples in Fig. 1 show an enrichment of ^{129}Xe from the decay[4, 8] of ^{129}I (half-life = 17 x 10^6 yr, but now extinct), one might expect the heavy xenon isotopes to contain a component of fission products from extinct ^{244}Pu (half-life = 82 x 10^6 yr). As the total amount of fissiogenic xenon generated from ^{244}Pu over the life span of the Earth is expected to exceed that from the spontaneous fission of ^{238}U by a factor[23] > 15 (if the Earth is contemporaneous with meteorites[3, 8]), we attribute the fission yields of xenon isotopes in natural gas to a mixture of fission products from ^{238}U and ^{244}Pu.

The xenon isotope ratios reported by Bennett and Manuel[7] have not been included in Table 1 or Fig. 1 because a quantitative correction for isotopic fractionation in the xenon from these gases cannot be made because of interference at m = 124, 126 and 128 (ref. 7). A recent report[24] of xenon in a terrestrial anorthosite shows an extremely high enrichment of ^{132}Xe. This anomaly cannot be accounted for by mass fractionation or spontaneous fission, and remains unexplained on the basis of our present understanding of xenon in natural gas.

In conclusion, it seems that most natural gases contain at least small enrichments of ^{129}Xe from the decay of (extinct) ^{129}I. Some of these gases also exhibit an enrichment of the heavier xenon isotopes, $^{131-136}$Xe, apparently a mixture of fission products from ^{238}U and ^{244}Pu.

This investigation was supported by a grant from the U.S. National Science Foundation. We thank Mr. B. Eklund of the Union Oil Company and Mr. G. E. McIver of the Mobil Research and Development Corporation for the natural gas samples.

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Table 1 Natural Gas Samples Analysed in This Study

Sample	G-1	G-2	G-3	G-4
Volume of sample (cc STP)	3.81	3.31	2.09	3.69
Well name	Gas from 17 wells collected at Lisbon unit, Plant # 28	Brown Bassett	Brown McNich ILT	Keith Mitchell
Location	San Juan Co., Utah	Terrel Co., Texas	Terrel Co., Texas	Terrel Co., Texas
Depth (ft.)	8000-9000	13,888-14,670	13,888-14,670	17,410-18,380
Formation	Mississipian Series	Ellenberger	Ellenberger	Ellenberger
Bottom hole press. (psi)		3,500	3,500	7,908
Bottom hole temp. (^{o}F)		261	261	275
Previous Analyses of Major Components in Volume Percent*				
N_2	19.8	0.38	0.37	0.41
CO_2	21.8	53.7	53.4	68.2
CH_4	50.4	45.5	45.8	30.8
Heavier hyrocarbons	8.00	< 1.0	< 1.0	< 1.0

*Analysis shown for G-1 is from Mr. B. Eklund (private communication) and analyses shown for the other gas samples are from Mr. G. E. McIver (private communication).

Table 2 Xenon in Natural Gas

Sample	G-1	G-2	G-3	G-4	CO_2-Rich Well Gas*		Navajo†	Air#
					I	II		
124	2.37 ± 0.02	2.35 ± 0.04	2.38 ± 0.03	2.42 ± 0.02	2.35 ± 0.10	2.41 ± 0.06	2.33 ± 0.04	2.35
126	2.24 ± 0.02	2.21 ± 0.02	2.25 ± 0.04	2.25 ± 0.02	2.25 ± 0.10	2.30 ± 0.06	2.20 ± 0.04	2.21
128	47.5 ± 0.4	47.6 ± 0.5	48.6 ± 0.6	46.8 ± 0.3	46.9 ± 0.5	47.5 ± 0.5	46.6 ± 0.04	47.0
129	654 ± 3	653 ± 5	651 ± 5	654 ± 3	711 ± 6	707 ± 4	651 ± 2	648
130	≡100	≡100	≡100	≡100	≡100	≡100	≡100	≡100
131	521 ± 2	521 ± 6	518 ± 4	517 ± 3	521 ± 5	524 ± 3	531 ± 3	519
132	668 ± 3	663 ± 6	659 ± 5	657 ± 2	677 ± 6	676 ± 5	706 ± 3	659
134	267 ± 1	258 ± 2	257 ± 2	256 ± 1	278 ± 2	279 ± 3	303 ± 1	256
136	230 ± 1	221 ± 1	219 ± 2	217 ± 2	241 ± 2	245 ± 3	275 ± 1	217
^{130}Xe content x 10^{-12} cc STP/cc gas	46.7	10.2	6.72	128	0.30	0.40	83.2	3,550

*Results reported by Boulos and Manuel[8]

†Results reported by Clarke and Thode[5]

#Results reported by Nier[9]

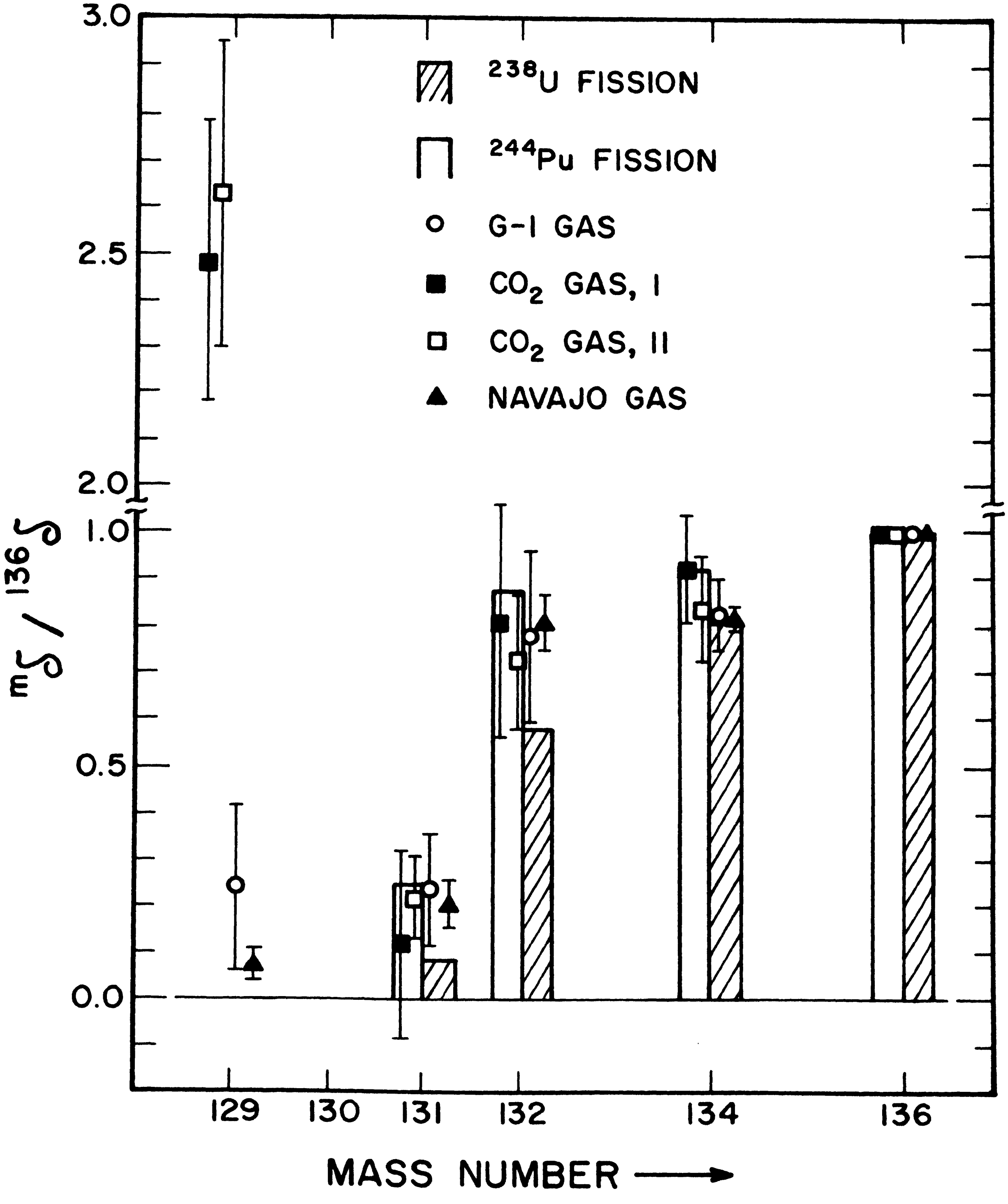
Table 3 Noble Gas Isotopic Ratios in Natural Gas

Gas	Air[†]	B-69[*]	C-17[*]	B-62[*]	C-16[*]
^{132}Xe/^{130}Xe	6.59	6.64	6.66	6.68	6.91
^{131}Xe/^{130}Xe	5.19	5.23	5.25	5.25	5.42
^{38}Ar/^{36}Ar	0.187	0.188	0.194	0.190	0.206
^{130}Xe/^{84}Kr	5.46×10^{-3}	6.94×10^{-3}	8.50×10^{-3}	11.7×10^{-3}	15.4×10^{-3}
^{130}Xe/^{36}Ar	1.13×10^{-4}	1.29×10^{-4}	3.98×10^{-4}	5.27×10^{-4}	12.7×10^{-4}

[†] Composition of air is from Veriani[25], and the isotopic composition of noble gases in air is from Nier[9,26].

[*] Results reported by Bennett and Manuel[7].

Fig. 1. A Comparison of ${}^{m}\delta/{}^{136}\delta$ ratios in natural gas sample G-1, (this study), in CO_2-rich gases (ref. 8), and in Navajo well gas (ref. 5) with the spontaneous fission yields reported for ${}^{238}U$ (ref. 10) and for ${}^{244}Pu$ (ref. 11).



3.0
2.5
2.0
1.0
0.5
0.0
$^m\delta / ^{136}\delta$
^{238}U FISSION
^{244}Pu FISSION
G-1 GAS
CO$_2$ GAS, I
CO$_2$ GAS, II
NAVAJO GAS
129
130
131
132
134
136
MASS NUMBER →

Fig. 1

IV. IODINE-129 IN THYROID GLANDS

Manuscript as submitted to *Science*.

Abstract. The amounts of ^{129}I present in mammalian thyroid glands have been determined by a combination of neutron activation and mass spectrometry. Contemporary thyroid glands contain $^{129}I/^{127}I \approx 10^{-8}$ and commercial I_2 contains $^{129}I/^{127}I \leq 10^{-10}$. The latter ratio probably reflects the lower detection limit of this technique.

Several investigators (1, 2) have noted the potential utility of ^{129}I as an isotopic tracer for the study of iodine pathways in biological and geological systems. This long-lived radioactive nuclide (half-life = 17×10^6 years) is produced in nature by spontaneous fission (3), by neutron capture reactions on tellurium (4), and by spallation reactions on xenon in the upper atmosphere (5). Recent technological processes have augmented the natural supply of ^{129}I on the earth's surface due to the production of ^{129}I from neutron induced fission of ^{235}U and ^{239}Pu in nuclear reactors and weapons.

Another fission produced iodine isotope, ^{131}I, has been used extensively as an iodine tracer in biological systems (6). This isotope has an 8 day half-life, which limits the effective "tracer" time for a given input of ^{131}I to a period of a few months and imposes a similarly short laboratory storage time on ^{131}I-labeled compounds. The use of long-lived ^{129}I as a tracer overcomes both of these difficulties. Further, radiation effects on a system are much lower when ^{129}I is used instead of ^{131}I; the specific radioactivity of ^{131}I is about a billion times that of ^{129}I and the energy released per decay is 5 times greater for ^{131}I than for ^{129}I. Nevertheless, there has been limited use of ^{129}I as a tracer due to experimental difficulties in determining quantitatively trace levels of ^{129}I.

Purkayastha and Martin (7) first noted the possibility of applying neutron activation analysis to the detection of ^{129}I by measuring the activity of the ^{130}I produced in the reaction, $^{129}I(n,\gamma)^{130}I$. Studier _et_ al. (2) and Edwards (5) pointed out that this technique makes it possible to use ^{129}I as a tracer, and Kohman and Edwards (8) list $^{129}I/^{127}I$ ratios in several terrestrial samples that have been measured by this technique. Recently Srinivasan et al. (9) employed high sensitivity noble gas mass spectrometry to measure the $^{129}I/^{127}I$ ratio in the mineral iodyrite (AgI), and their results suggest that the $^{129}I/^{127}I$ ratio in this ore is about 100, 000 times smaller than the tentative value obtained radiochemically by counting neutron activated ^{130}I (8).

In view of the fact that previous work in our laboratory has demonstrated the high sensitivity obtainable by combining neutron activation analysis with noble gas mass spectrometry (10,11), it was decided to apply this analytical technique to the development of a reliable detection method for tracer quantities of ^{129}I. The procedure involves mass spectrometric measurement of stable xenon isotopes which are produced by the following neutron capture reactions on iodine containing both ^{129}I and ^{127}I:

$$^{127}I(n,\gamma)^{128}I \xrightarrow[25\ \text{min}]{\beta^-} {}^{128*}Xe \quad (1)$$

$$^{127}I(n,2n)^{126}I \xrightarrow[13\ \text{d}]{\beta^-} {}^{126*}Xe \quad (2)$$

$$^{129}I(n,\gamma)^{130}I \xrightarrow[12.4\ \text{hr}]{\beta^-} {}^{130*}Xe \quad (3)$$

$$^{127}I(n,\gamma)^{128}I(n,\gamma)^{129}I(n,\gamma)^{130}I \xrightarrow[12.4\ \text{hr}]{\beta^-} {}^{130*}Xe \quad (4)$$

The xenon isotopes produced by either reaction (1) or reaction (2) can be used to monitor the stable iodine isotope, ^{127}I, while the $^{130*}Xe$ produced by reaction (3) monitors the ^{129}I. For a given irradiation, both the $^{130*}Xe/^{128*}Xe$ ratio and the $^{130*}Xe/^{126*}Xe$ ratio resulting from reactions (1)-(3) will be proportional to the $^{129}I/^{127}I$ ratio in the sample. Thus, a single mass spectrometric measurement of these stable xenon isotopes in iodine samples which have been exposed to identical irradiations will show the relative $^{129}I/^{127}I$ ratio in each sample. Reaction (4) shows that the detection limit for ^{129}I by this technique will depend on the probability of three successive neutron capture reactions on ^{127}I.

In order to demonstrate the sensitivity of the proposed method, we have measured xenon isotopes in neutron-irradiated iodine which had been extracted from the thyroids of mammals. Information on the thyroids used in this study is given in Table 1. The ovine thyroids were dried, powdered samples which had been collected in Nashville, Tennessee in 1964-1967. These were supplied for our study by Professor Van Middlesworth of the University of Tennessee Medical College in Memphis. The bovine thyroids were obtained fresh from slaughter houses in San Francisco, California. Fresh human thyroids were provided by the Medical Schools of Washington University and St. Louis University in St. Louis, Missouri, and by the Boone County Hospital in Columbia, Missouri.

The last column in Table 1 gives the total number of thyroids represented in each sample. Iodine was extracted from thyroids using the method described by Kohman and Edwards (8). The iodine from aliquots of the ovine glands and the total iodine extracted from human and bovine glands were used in the irradiations.

The iodine samples and monitors of reagent grade iodine were irradiated for 12 hours at a flux of 1×10^{14} n cm^{-2} sec^{-1}. For samples with a high $^{127}I/^{129}I$ ratio, the irradiation produces a $^{128*}Xe/^{130*}Xe$ ratio that is too large for mass spectrometric measurement. Since very high $^{127}I/^{129}I$ ratios were expected in these samples, the irradiated iodine was dissolved to remove the $^{128*}Xe$ and precipitated as PdI_2 approximately 12 hours after the end of the irradiation. This procedure reduced the $^{128*}Xe$ to a level which permitted the mass spectrometric measurement of $^{128*}Xe$, $^{126*}Xe$ and $^{130*}Xe$ (the decay products from ^{128}I, ^{126}I and ^{130}I, respectively, which remained 12 hours after the irradiation) with complete resolution of each mass number.

The PdI_2 was allowed to accumulate radiogenic xenon isotopes for approximately one month before extraction of the xenon for mass spectrometric analysis. The amounts of $^{128*}Xe$ released from the PdI_2 were 10^3-10^4 times higher than the amounts of ^{128}I expected to remain 12 hours after the irradiation, apparently due to adsorption or occlusion of $^{128*}Xe$ during the precipitation of PdI_2. For this reason the $^{126*}Xe/^{130*}Xe$ ratio was used as a monitor of the $^{127}I/^{129}I$ ratio in the samples.

Table 2 gives the results of our analyses for xenon in the PdI_2 samples. Two separate irradiations were conducted and xenon from the PdI_2 precipitates of the two irradiations was analyzed at different times using the mass spectrometer. The irradiation used with each sample is indicated in column two (Table 2). Large variations in the sensitivity of the mass spectrometer during analyses of xenon from irradiation No. 1 resulted in larger uncertainties in the $^{129}I/^{127}I$ ratios measured from this irradiation. Column three lists the measured $^{126*}Xe/^{128*}Xe$ ratios. The uncertainties in these values generally increase as the amount of $^{126*}Xe$ or $^{130*}Xe$ decrease. Hence, the larger statistical errors in the $^{126*}Xe/^{130*}Xe$ ratios generally correspond to samples containing small amounts of thyroid iodine. The large statistical errors in the $^{126*}Xe/^{130*}Xe$ ratios in the monitors reflect the low ^{129}I content of this iodine relative to that of thyroid iodine.

In order to calculate the $^{129}I/^{127}I$ ratios given in the last column of Table 2 from the $^{126*}Xe/^{130*}Xe$ ratios given in the second column, the following procedure was followed.

(1) The observed amount of $^{130*}Xe$ was corrected for the amount of $^{130*}Xe$ which decayed during the 12-hour period after the irradiation to obtain the amount of ^{130}I at the end of the irradiation. The actual precipitation time of each sample had been recorded, and correction factors were calculated for a 12.4 hour half-life of ^{130}I (12). These corrections ranged from 1.59 to 1.87.

(2) The observed amount of $^{126*}Xe$ was corrected for the

amount of ^{126}I remaining in each sample at the time of xenon analysis in order to obtain the amount of ^{126}I which was present when PdI_2 was precipitated. Using a half-life of 13.0 days for ^{126}I (12), the correction factors on $^{126*}Xe$ ranged from 0.691 to 0.871. Variations in the precipitation time of PdI_2 for the different samples were negligible relative to the half-life of ^{126}I, and no corrections were made on ^{126}I for these small differences in precipitation times.

(3) The amount of ^{127}I in each sample was calculated from the amount of ^{126}I present when PdI_2 was precipitated relative to the amount of ^{126}I present when PdI_2 was precipitated for the corresponding monitor. The PdI_2 from each monitor had been weighed as $PdI_2.H_2O$ after drying for 30 minutes at 110°C.

(4) Since the amount of $^{130*}Xe$ in the monitors was very low and probably due to triple neutron capture on ^{127}I [See the earlier discussion on reaction (4)], the amount of ^{129}I in the samples cannot be calculated from a direct comparison of their $^{130*}Xe$ content with that in the monitors. The amount of ^{129}I present in each sample was therefore calculated from the amount of ^{130}I present at the end of the irradiation assuming the thermal neutron cross section of ^{129}I to be 27 barns (12) and the half-life of ^{130}I to be 12.4 hours (12).

The last column in Table 2 shows the $^{129}I/^{127}I$ ratios present in the thyroid glands analyzed in this study. The error shown on each $^{129}I/^{127}I$ ratio represents one standard deviation and includes errors in the measurement of the $^{126*}Xe/^{130*}Xe$ ratio and errors in the measurement of the xenon content of monitors and samples. Any systematic errors in the half-lives, cross sections, etc. are not represented in Table 2. In general the amount of iodine recovered from fresh thyroid glands was low, and our results show a correspondingly large uncertainty in the $^{129}I/^{127}I$ measurement. However, our results on sheep thyroid iodine show that the method we have employed can measure the relative $^{129}I/^{127}I$ ratios with a reliability of ± 10% in 40-50 mg samples of iodine containing about 5×10^{-10} g of ^{129}I.

From the amount of $^{130*}Xe$ produced on the monitors, we estimate a lower detection limit for this technique of $^{129}I/^{127}I \approx 10^{-10}$. Assuming a thermal neutron capture cross section of 6.2 barns for ^{127}I (12) and 24 barns for ^{129}I (12), we estimate that the total $^{130*}Xe$ in these monitors could be due to triple neutron capture on ^{127}I. The results obtained for monitor No. 8 would require a thermal neutron capture cross section of ^{128}I equal to 65 ± 45 barns, and the results from monitor No. 7 would require a cross section of 21 ± 11 barns.

In conclusion, the results of this initial application of neutron activation and noble gas mass spectrometry to the problem of ^{129}I detection suggest that about 5×10^{-10} g of ^{129}I can be detected with a reliability of ± 10%. Using a neutron flux of 10^{14} n cm^{-2} sec^{-1}, the detection limit of this technique corresponds to $^{129}I/^{127}I \geq 1 \times 10^{-10}$. It is conceivable that this $^{129}I/^{127}I$ ratio represents the isotopic composition of iodine in the iodine monitors, but the *in situ* production of ^{129}I during the irradiation by double neutron capture on ^{127}I seems a more plausible explanation. Our results indicate that tracer levels of ^{129}I corresponding to less than 0.1 pico curie of low energy radiation can be reliably measured by the method used in this study (13).

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13. This investigation was supported by NSF grant NSF-GA-16618. We are grateful to Professor L. Van Middlesworth, of the University of Tennessee Medical College in Memphis, for his generosity in supplying these excellent samples of sheep thyroid powder. We thank Dr. John Kissane and Ms Nancy Martin of Washington University, St. Louis, Mo., Dr. Harold McCartney of St. Louis University, St. Louis, Mo., and Dr. Gammel of Boone County Hospital, Columbia, Mo., for assistance in obtaining the human thyroid glands. We also thank Dr. D. McKown, Mr. J. Schlapper and Mr. D. Grey of the Nuclear Reactor Facility of the University of Missouri-Columbia for their cooperation and assistance with irradiation of the samples.

TABLE 1. ANIMAL THYROID GLANDS ANALYZED IN THIS STUDY

Species	Sample No.	Extraction Date of Thyroids	Source	Number of Glands in Sample
Sheep	S-4	April 29-Sept. 3, 1964	Nashville, Tenn.	187
Sheep	S-5	June 24-Oct. 21, 1966	Nashville, Tenn.	158
Sheep	S-6	Nov. 8, 1966-March 10, 1967	Nashville, Tenn.	173
Cattle	C-2	December, 1971	San Francisco, Calif.	22
Cattle	C-1	December, 1971	San Francisco, Calif.	28
Human	H-4	December, 1971	St. Louis & Columbia, Mo.	7
Human	H-3	January, 1972	St. Louis, Mo.	5

TABLE 2. IRRADIATION AND MASS SPECTROMETRIC ANALYSIS OF THYROID IODINE

Sample No.	Irradiation No.	$^{126*}Xe/^{130*}Xe$ Observed	Final Weight of Iodine Analyzed	$^{129}I/^{127}I \times 10^9$ Calculated
S-4	2	151 ± 2	40.1 mg	13.8 ± 1.1
S-5	1	568 ± 13	44.4 mg	6.8 ± 3.5
S-6	2	241 ± 18	53.1 mg	8.9 ± 0.7
C-2	2	200 ± 11	13.5 mg	10.5 ± 0.9
C-1	1	1,135 ± 465	1.2 mg	3.2 ± 2.1
H-4	1	182 ± 26	0.3 mg	12 ± 6
H-3	1	709 ± 4,254	0.4 mg	5 ± 33
M-7 (Monitor)	2	38,750 ± 19,375	67.2 mg	(0.06 ± 0.03)
M-8 (Monitor)	1	24,000 ± 12,480	101.7 mg	(0.18 ± 0.13)

V. APPENDICES

APPENDIX A

Preparation of Natural Gas Samples for Mass Spectrometric Analysis

PREPARATION OF NATURAL GAS SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

The object of the present analysis of natural gas samples was to accurately determine the isotopic compositions and concentrations of xenon and krypton. The procedures can be summarized as follows.

(1) Field sampling of the natural gas wells: Stainless steel cylinders with valves at both ends were used to collect the natural gas samples from their respective fields. Keeping both valves open, each cylinder was first flushed for approximately 15 minutes with gas before closing one end valve and filling to a pressure of 450 to 650 psi. This flushing procedure was necessary in order to avoid any atmospheric contamination of the gases during sampling.

(2) Preparation of gas samples in a size adequate for mass spectrometric analysis: The high sensitivity mass spectrometer employed in these analyses has an optimum detection in the range of 10^{-9} to 10^{-13} cm^3 STP of xenon. It was thus important to prepare samples with a xenon content within that range.

Figure 1 is a schematic diagram of the vacuum system. The stainless steel cylinder, A, was connected to a flexible Swagelok metal hose, B, which could withstand pressures of up to 1, 760 psi. The valves V-1, V-2 and V-3 were all stainless steel and could hold pressures up to 1, 000 psi as well as withstand the bake-out temperatures reached in vacuum work. A metal to Kovar-glass seal, C, was used to connect V-3 to the rest of the system which was mostly fabricated of Pyrex glass. A manometer, D, consisted of an 80 cm long capillary tubing which dipped into a mercury trough. The Pyrex bulb, F, was added to increase the volume of the system while E was an ion gauge used to measure the initial pressure of the system. A bakeable Bayard-Alpert type valve, V-4, connected the vacuum system to a mercury diffusion pump and a mechanical fore pump. The vacuum system was separated from the diffusion pump by a liquid nitrogen trap while the diffusion pump was separated from the fore pump by a dry ice trap. A set of calibrated Pyrex glass ampoules, G, were attached to the vacuum system through capillary tubing, each ampoule having a break-seal on the opposite end for subsequent use in attaching the ampoules to the mass spectrometer system. Ampoules of two volume ranges were employed; one set was 3-6 cm^3 and the second set 100-110 cm^3.

The vacuum system was first baked-out to remove all adsorbed atmospheric gases. The ampoules were filled with the gas being sampled by trapping a small amount of gas in the flexible metal hose, then allowing that volume of gas to expand into the rest of the system. Emptying the cylinder in this fashion ensured the prevention of any mass fractionation of the gases during their expansion. To further eliminate atmospheric contamination, the system was flushed three times with the gas being sampled.

An outline of the gas sampling procedure is as follows:

(i) Close V-3 and V-4, then open V-2 wide, leave for 15 minutes to equilibrate.

(ii) Close V-2 and open V-3 allowing the gas to expand into the system.

(iii) Leave the gas to equilibrate in the system for 15 minutes then open V-4 to pump the gases from the system.

(iv) Repeat steps (i) to (iii) three times then seal off two ampoules to be used as system blanks.

(v) Repeat steps (i) and (ii).

(vi) Allow the gas to equilibrate in the system for five to six hours, then seal ampoules at the calibration mark along the capillary tubing. Pressures during sealing were in the 10-20 torr range.

The samples thus prepared were ready for mass spectrometric analysis as described in Appendix C.

Fig 1. Vacuum System for Preparation of Natural Gas Samples

A. Stainless Steel Cylinder

B. Flexible Metal Hose

C. Metal to Kovar-glass Seal

D. Manometer

E. Ion Gauge

F. Pyrex Bulb

G. Calibrated Ampoules

V-1, V-2 and V-3: Stainless Steel Valves

V-4: Bayard-Alpert Valve

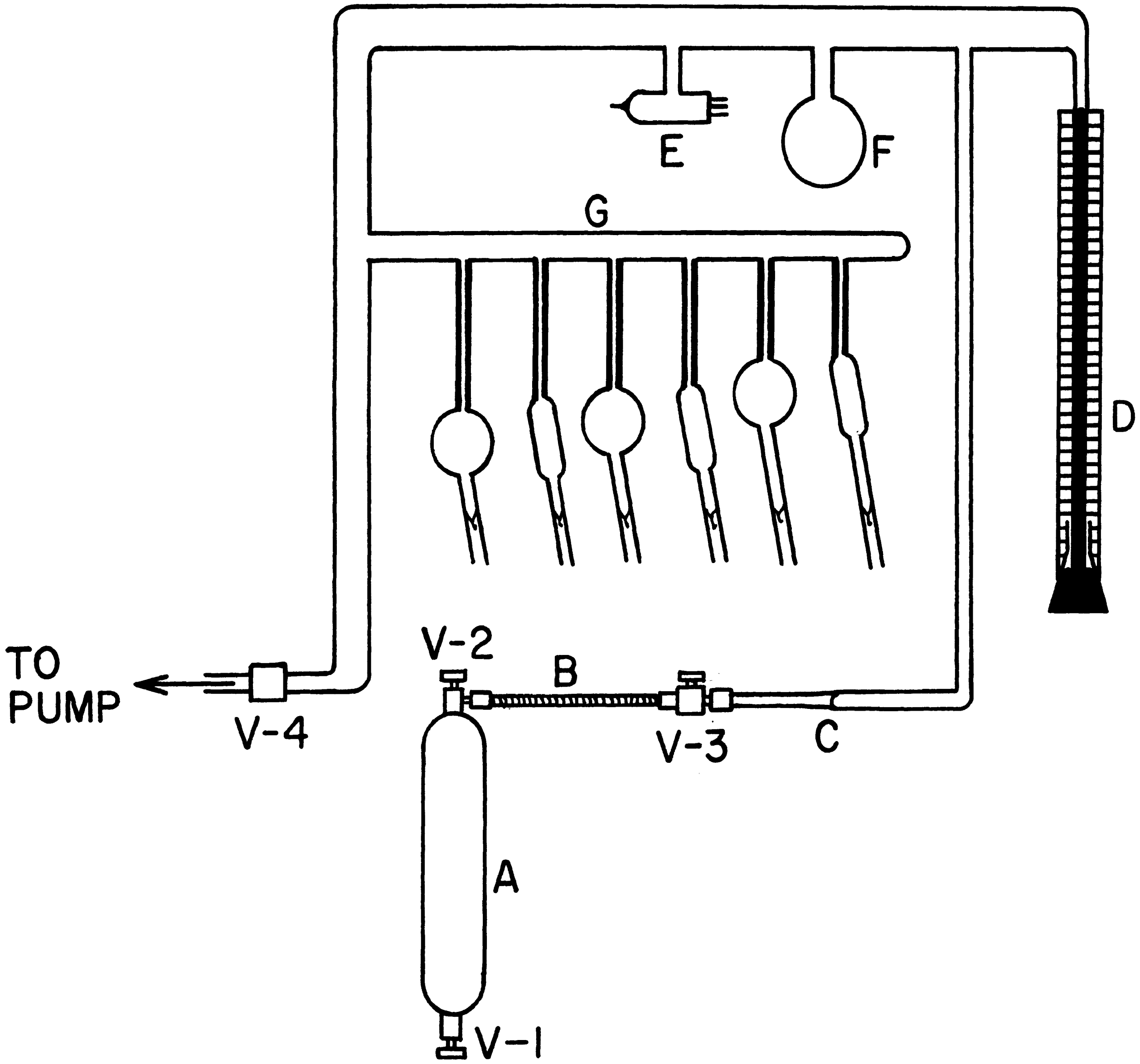

Fig. 1

APPENDIX B

Extraction and Neutron Activation Analysis of the Iodine in Animal Thyroid Glands

EXTRACTION AND NEUTRON ACTIVATION ANALYSIS OF THE IODINE IN ANIMAL THYROID GLANDS

The object of this research was to determine the present levels of radioactive ^{129}I, a long-lived fission product of nuclear reactors and weapons, in the biological cycle. Animal thyroid glands were chosen for analysis since they contain most of the iodine retained by the animal body. On irradiating thyroid iodine with a thermal neutron flux, the following reactions take place: $^{127}I(n,\gamma)^{128}I$ and $^{129}I(n,\gamma)^{130}I$. Both ^{128}I (half life of 25 minutes) and ^{130}I (half life 12.5 hours) decay to the stable xenon isotopes, ^{128}Xe and ^{130}Xe, respectively. High energy neutrons, which exist near the reactor fuel elements, induce the nuclear reaction, $^{127}I(n,2n)^{126}I$; the ^{126}I decays with a half life of 13 days to stable ^{126}Xe. By means of a Reynolds' type high sensitivity mass spectrometer, the relative amounts of ^{130}Xe, ^{128}Xe and ^{126}Xe could be determined with a high degree of accuracy.

Three types of thyroid glands were analyzed: human, bovine and sheep. In each case the iodine was extracted from the tissue and precipitated as palladium iodide. The PdI_2 was then decomposed and the free iodine allowed to react with aluminum metal forming Al_2I_6, the chemical compound of iodine used for the irradiation. Six thyroid iodine samples together with two iodine monitors were irradiated in the reactor flux trap for 12 hours at a thermal neutron flux of 1×10^{14} neutrons per second per cm^2. Approximately eight to ten hours after the end of the irradiation the samples were dissolved in water and the iodine reprecipitated with excess Pd(II) and weighed as $PdI_2.H_2O$. The precipitates were then sealed under vacuum in separate glass ampoules. After allowing an adequate decay interval, the decay products of ^{126}I, ^{128}I and ^{130}I were measured mass spectrometrically as ^{126}Xe, ^{128}Xe, and ^{130}Xe, respectively.

Extraction of Iodine From Thyroid Tissue

Both bovine and human thyroid tissues were obtained freshly frozen, while the sheep tissue was obtained as 'thyroid powder'. The latter is produced from thyroid glands which have been dried and powdered. Approximately 90 g of the specimen was wet-ashed with approximately 50 g NaOH and 10 g Na_2CO_3. The mixture was then dissolved and the solution cleaned by filtration. Sodium bisulphite (0.05 M) was added to reduce all forms of iodine to the iodide ion (I^-). The iodide was then oxidized by means of $NaNO_2$ (1 M) to I_2 which was extracted into CCl_4; this oxidation process was repeated at least three times to insure the complete extraction of the iodine. Free iodine was then reduced to I^- with $NaHSO_3$ (0.05 M), extracted into the aqueous phase, and precipitated as PdI_2 in the presence of excess Pd(II).

The PdI_2 was filtered on tared glass-fiber filter paper, then dried in a vacuum oven at 100°C and weighed as PdI_2. Drying in a nonvacuum oven results in the formation of $PdI_2.H_2O$.

Preparation of Samples for Irradiation

The precipitation of thyroid iodine as PdI_2 has two advantages, the first being that iodine is the only halide that forms an insoluble palladium salt, and the second is the ease by which PdI_2 can be decomposed yielding free iodine. This latter property was useful in the preparation of the samples for irradiation. Aluminum iodide was chosen as the form of thyroid iodine for the irradiation since aluminum gives rise to short-lived radioactivities only.

The filter papers containing the PdI_2 from a sample of thyroids were placed in a glass system, the pressure was reduced to $\approx 10^{-3}$ torr, and the PdI_2 was heated to 350°C. The I_2 vapors that evolved were condensed on pure aluminum metal beads which had been placed in a glass finger cooled with liquid N_2. The decomposition was continued for two hours, after which the Al-beads plus I_2 were sealed (still under vacuum). In order to convert all I_2 into Al_2I_6, the glass ampoule was heated to 180°C and allowed to cool to room temperature. The Al-beads plus Al_2I_6 were then removed from the glass ampoule, wrapped in a piece of Al-foil (weighing ≈ 0.11 g), placed in a quartz vial, and sealed under partial vacuum.

Preparation of Iodide Irradiation Monitors

Approximately 0.2 g aluminum beads plus 0.1 g pure iodine metal were sealed in a Pyrex glass tube under vacuum. These ampoules were heated to 180°C and allowed to cool forming Al_2I_6 on the surfaces of the Al-beads. The Al plus Al_2I_6 was then wrapped in Al-foil, placed in quartz vials, and sealed under partial vacuum.

Irradiation by Thermal Neutrons

The quartz vials containing the thyroid iodine samples and monitors where sealed in Al-cans and placed in the flux trap of the reactor at the University of Missouri-Columbia. They were irradiated for 12 hours in a thermal neutron flux of 1×10^{14} neutrons per second per cm^2.

Post-Irradiation Chemistry

Seven hours after the end of irradiation the outer Al-cans and quartz vials were opened, and then each inner Al-foil containing the Al-beads plus Al_2I_6 was placed in a labeled beaker containing 15 ml of H_2O. The Al-foils were shredded by means of forceps and the excess Al removed by filtration. Nitrogen gas was then bubbled through the solution for 15 minutes so as to sweep out radiogenic ^{128}Xe that had formed. The iodide was then precipitated as PdI_2 with excess Pd(II), filtered on glass-fiber filter paper, then dried and weighed as $PdI_2.H_2O$. Each precipitate was placed in a separate glass Pyrex ampoule with a break-seal at one end for attachment to the mass spectrometer system and all ampoules were attached to a vacuum system. After the pressure was reduced to $\approx 10^{-3}$ torr, each ampoule was sealed and then allowed to accumulate radiogenic ^{126}Xe, ^{128}Xe and ^{130}Xe for mass spectrometric analysis.

APPENDIX C

Mass Spectrometric Analysis

MASS SPECTROMETRIC ANALYSIS

A high sensitivity mass spectrometer especially designed for noble gas analysis was used in the measurement of the isotopic compositions and concentrations of xenon and krypton. The spectrometer tube is made of Pyrex glass with a 4.5 inch orbit radius, a source slit width of 0.012 inches, and a collector slit width of 0.024 inches. With such parameters, the spectrometer has a resolving power sufficient to adequately separate adjacent xenon isotopes of comparable abundance, and has a sensitivity as high as 0.5×10^6 atoms of xenon. A separate source magnet is used; this provides a guide field of 100 gauss paralled to the electron beam, thus improving on the efficiency of the ion source. The ion detector is a nine-stage electron multiplier. A more detailed description of this mass spectrometer was given by Reynolds [J. H. Reynolds, Rev. Sci. Instr. 27, 928 (1956)].

The spectrometer tube is evacuated through a Bayard-Alpert type valve which is capable of holding a high vacuum and can withstand high temperature bake-out. Vacuum is attained by means of a two-stage mercury diffusion pump coupled with a mechanical fore pump; a liquid nitrogen trap separates the system from the diffusion pump while a dry ice trap separates the diffusion and fore pumps. Ultra-high vacuum is obtained after baking out the vacuum system at 300°C for ≈ 12 hrs. Pressures in the order of 10^{-9} torr are routinely obtained.

Noble gas analysis is carried out by static operation of the instrument, where the tube is isolated from all pumping before admitting the gas sample. An advantage of the static method as compared to the flow method of analysis is in the elimination of interference due to hydrocarbon contamination, the hydrocarbons being decomposed by the hot filament in the ion source.

During the xenon and krypton analyses, the filament's emission current was maintained at 2 milliamperes and the ionizing electrons from the filament were accelerated through 80 volts. The ions were accelerated through 2000 volts in the spectrometer source, and the nine-stage electron multiplier was operated at 2000 volts.

A schematic diagram of the mass spectrometer plus the adjoining gas purification and separation systems is given in Figure 2. The valve, V-3, separates the mass spectrometer from the purification and separation systems, the vacuum on each side being produced by a separate set of diffusion and mechanical pumps; V-1 isolates the purification and separation systems.

Ampoules containing the samples to be analyzed were attached via break-seals to the purification system at C together with calibrated air spikes of volumes in the 0.016 cm^3 STP range. After reducing the pressure of the system to $\approx 10^{-9}$ torr, V-1 was closed and the sealed ampoules broken by means of iron slugs. In the case of natural gas samples, this was sufficient to release the gases into the purification system.

However, in the case of thyroid iodine (which was in the form of PdI_2), the ampoules containing the PdI_2 were attached to the purification system via a dry ice trap. After breaking the ampoule open to the system, the PdI_2 precipitate at the bottom of the ampoule was heated to 400°C thus decomposing and releasing I_2 together with all other gases held by the PdI_2; heating was continued for one hour. All the I_2 vapors condensed out on the walls of the dry ice trap, leaving the xenon and other noncondensible gases free in the system.

The noncondensible gases thus released were cleaned simultaneously on copper oxide at 550°C and on titanium at 850°C for two hours. After cooling, they were allowed into the gas separation section (V-2 being closed) by adsorption on a charcoal finger, G, at the sublimation temperature of CO_2 (-78°C); at this temperature only the krypton and xenon were adsorbed and the He, Ne and Ar were removed by opening V-1 for 30 minutes. With both V-1 and V-2 closed, the krypton and xenon were then driven off the charcoal and purified once more using a second titanium furnace, F, at 850°C. After cooling this second titanium to room temperature, the gases were ready for mass spectrometric analysis.

For natural gas samples, the xenon was selectively adsorbed on the charcoal at -33°C (the temperature was maintained by placing frozen mercury around the charcoal finger) while the krypton was allowed into the mass spectrometer for analysis. After analysis, the krypton was pumped out via V-4 while the xenon was driven off the charcoal at 150°C and then allowed into the mass spectrometer for analysis. No isotopic anomalies of krypton were observed in the natural gas samples.

In the case of thyroid iodine, both krypton and xenon were allowed into the mass spectrometer together, but only the xenon isotopes were analyzed since those are the only isotopic ratios of interest.

The mass spectrometer was calibrated with an air-spike of known volume before and after each analysis of natural gas. Blank analyses were run periodically to determine the amount of background in the system.

The mass spectrometer photomultiplier is attached to a Honeywell Brown recording potentiometer; the design is such that each peak height is proportional to the amount of isotope present. During the course of analysis, there is some change in the amount as well as isotopic composition of the gas due to the mass spectrometer self-pumping action and memory effects, respectively. In order to correct for this effect, it is necessary to extrapolate the spectrum to zero time (the time of gas entry into the mass spectrometer); the isotopic spectrum of each gas having been recorded nine times during the analysis.

The relative isotopic composition of a sample is obtained by extrapolation to zero time by means of a Fortran IV computer program written for an IBM 360 computer. A reference isotope is chosen, then the program linearly interpolates the height of this reference isotope at the time that each nonreference isotope was measured; it then linearly extrapolates the resulting ratios to zero time by the method of least-squares. The program also calculates the statistical error of each ratio based on the deviation of the experimental ratios from the least squares line.

To obtain the total concentration of each gas, the peak height of the reference isotope in the sample is compared with the average peak heights of the same isotope in the air spikes analyzed.

Fig. 2. Mass Spectrometer Plus Adjoining Gas Purification and Separation Systems

A. Titanium Furnace No. 1

B. Cu/CuO Furnace

C. Air Spikes

D. Samples Being Analyzed

E. Sample Ion Gauge

F. Titanium Furnace No. 2

G. Charcoal Finger

H. Mass Spectrometer Ion Gauge

T-1 and T-2: Dry Ice Traps

V-1, V-2, V-3 and V-4: Bayard-Alpert Valves

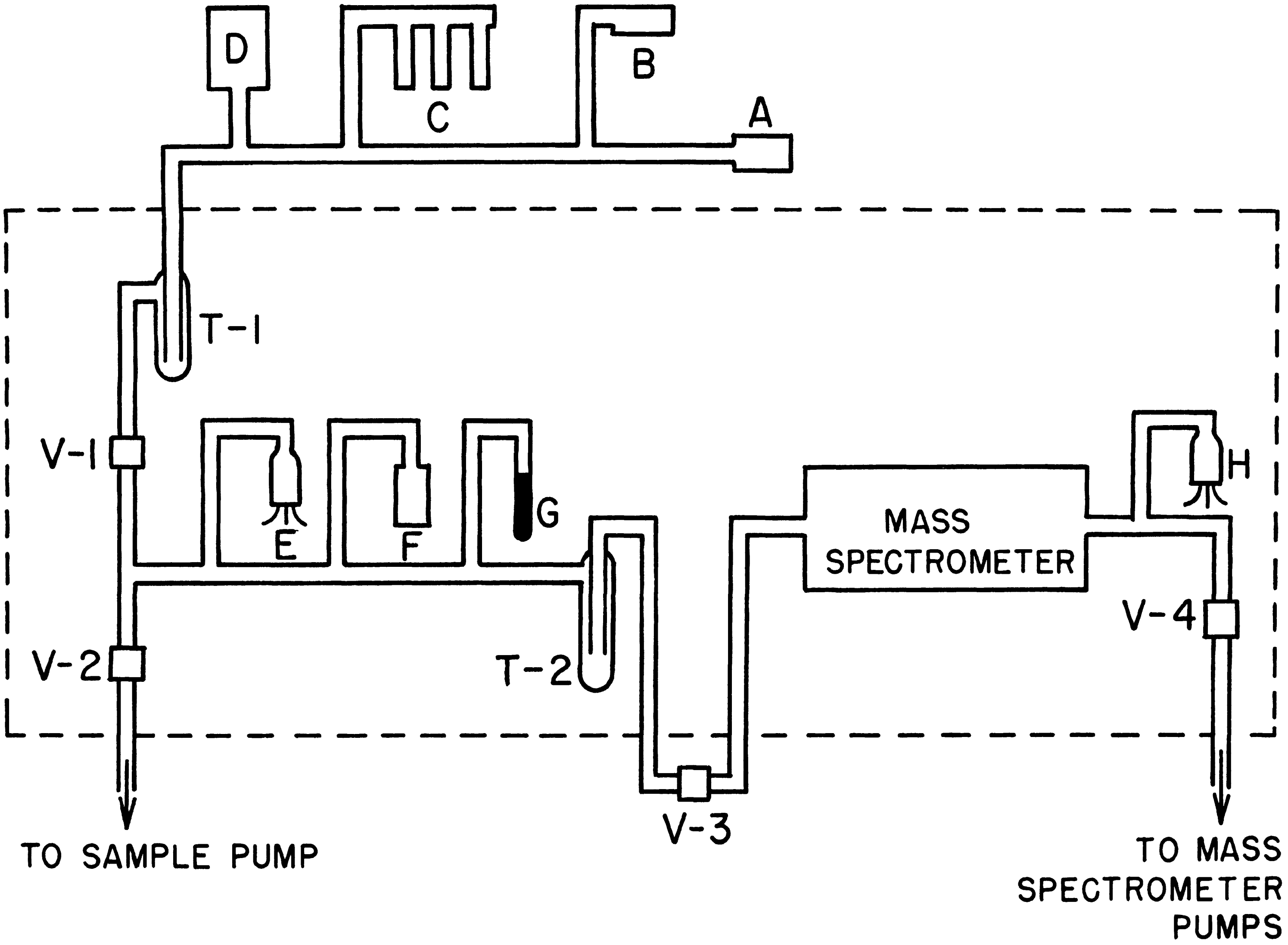
D
C
B
A
T-1
V-1
E
F
G
H
MASS SPECTROMETER
T-2
V-2
V-3
V-4
TO SAMPLE PUMP
TO MASS SPECTROMETER PUMPS

Fig. 2

VITA

Mervet Saleh Boulos was born and raised in Cairo, Egypt, daughter of Maurice A. Saleh, Civil Engineer, and Marcelle Tewfic. She received elementary education mostly in Egypt with two years in London, England; she received secondary education at The English School, Heliopolis, Cairo. In 1964 she obtained a B.S. degree in Chemistry and Physics from Cairo University, and in 1967 she obtained an M.S. degree in Solid State Science from The American University in Cairo. In 1967 she was married to Edward N. Boulos of Cairo, Egypt, who is a Ph.D. graduate of the University of Missouri-Rolla, USA. They presently have one daughter, Nermine.

Mervet entered the Graduate School at the University of Missouri-Rolla in 1968 as a teaching assistant in the Chemistry Department and has engaged in graduate study since that time.