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Isotopic anomalies of noble gases in natural gas

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ISOTOPIC ANOMALIES OF NOBLE GASES IN NATURAL GAS

BY

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A

THESIS

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ABSTRACT

Analyses of noble gases from four natural gases reveal radiogenic He$^4$ and Ar$^{40}$, excess Ne$^{21}$ and Ar$^{38}$ from α-induced reactions, and an excess of the β-unshielded xenon isotopes with an abundance pattern unlike that from the spontaneous fission of U$^{238}$. The pattern of excess Xe$^{129}$, Xe$^{131}$, Xe$^{132}$, Xe$^{134}$ and Xe$^{136}$ in these gas samples is such that a mixture of this xenon with the primordial xenon in meteorites could produce the abundance pattern of atmospheric xenon for all isotopes heavier than Xe$^{128}$. It is suggested that the heavy xenon isotopes in natural gas results from symmetric fission of a transuranium element near mass number 270.
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I. INTRODUCTION

This investigation of the abundance and isotopic composition of noble gases in helium-rich gas wells was undertaken in order to obtain new data which might be used to elucidate the origin of isotopic anomalies of noble gases in the atmosphere. Since noble gases are presently leaking to the atmosphere (Damon and Kulp, 1958a; Bieri et al., 1967) the isotopic composition of the present atmosphere is not static. The direction of change, and ultimately the origin of anomalous noble gases, might therefore be discovered in studying the noble gases presently leaking from the earth. Since the two major noble gas isotopes generated within the earth today are radiogenic $\text{He}^4$ and $\text{Ar}^{40}$, these two gases can be used as tracers to show that a sample contains noble gases leaking from the earth. The primary objective of this study was to accurately determine the isotopic composition of other noble gases accompanying these two tracer isotopes to see if they might contain evidence of the direction of evolution of the noble gases in the atmosphere.
II. LITERATURE REVIEW

The noble gases have great chemical inertness and high volatility at low temperatures. These characteristics have resulted in a well-documented depletion of the noble gases in terrestrial and meteoritic material (Suess, 1949, 1963; Brown, 1949; Reynolds, 1960b; Goles and Anders, 1961; Canals et al., 1968; Suess and Urey, 1956; Manuel and Rowe, 1964; Signer and Suess, 1963). The mass fractionation pattern across the noble gases has been used to estimate the conditions during the separation of these elements from the more condensable matter (Brown, 1949; Suess, 1949). Suess (1949), comparing atmospheric and solar abundances, noted that the atmosphere had retained only one out of every \(10^7\) atoms of xenon, and less than one of every \(10^{11}\) atoms of neon.

Suess (1949) found that the ratio of atmospheric to solar abundances of the noble gases fit the equation:

\[
-\log \left( \frac{N_{\text{terr}}}{N_{\text{sol}}} \right) = 7.1 + 10e^{-0.045M}
\]

Here \(N_{\text{terr}}\) is the terrestrial abundance of a non-radiogenic noble gas of mass \(M\). \(N_{\text{sol}}\) is the solar abundance of this noble gas. In making this calculation, Suess assumed that the atmosphere contained the earth's entire inventory of noble gases.

Suess (1949) suggested that the fractionation pattern of atmospheric noble gases resulted from an early uniform loss to about \(10^{-7}\) of the initial abundance by hydrodynamic flow, followed by selective diffusion from the earth's gravitational field.
In the same year, working independently, Brown (1949) also noted the depletion of atmospheric noble gases. He suggested that the absence of similar depletions for \( \text{H}_2\text{O}, \text{N}_2, \text{CO}_2 \) and \( \text{O}_2 \) resulted from chemical retention of these atmospheric components during the earth's formation. On this basis he concluded that the present atmosphere is of secondary origin, i.e. the result of chemical processes liberating these gases subsequent to the formation of the earth itself. Recent results from this laboratory by Canals et al. (1968) have been interpreted as evidence that even the noble gases in the atmosphere today have leaked from the earth over geological time.

In addition to recording the separation of noble gases from other elements as a mass fractionation pattern, the isotopic composition of residual noble gases has since been easily altered by nuclear reactions. Investigations of the isotopic anomalies of noble gases have been used to determine the "age" of terrestrial rocks and minerals, and the concentrations of radiogenic gases in the atmosphere have been used to estimate the rate of degassing of the earth (Turekian, 1958; Shillibeer and Russell, 1955; Patterson, 1956; Damon and Kulp, 1958a, 1958b; Gerling and Shokaliukov, 1959, Gerling et al., 1959; Butler et al., 1963; Wasserburg et al., 1963; Funkhouser and Naughton, 1963; Manuel, 1962; Rankama, 1954; Shillibeer and Russell, 1955; Signer and Suess, 1963).

The French geochemist Moureau (1923), concluded as early as the 1920's that the \( \text{He}^4 \) in our present atmosphere is of radiogenic, rather than primordial, origin. Weizäcker (1937) first suggested that atmospheric \( \text{Ar}^{40} \) was due to the decay of terrestrial \( \text{K}^{40} \).
Many additional studies have supported the radiogenic origin of $^{4}\text{He}$ and $^{40}\text{Ar}$ (Morrison and Beard, 1949; Morrison and Pine, 1955; Pierce, 1960; Ruedemann and Oles, 1929; Wells, 1929; Wasserburg et al., 1957; Wasserburg and Mazor, 1964; Wasserburg et al., 1963; Faul et al., 1952; Stroud et al., 1967; Clarke and Thode, 1964; Zartman et al., 1961). Zartman et al. (1961) noted that variations in the ratio of $^{4}\text{He}/^{40}\text{Ar}$ in natural gas from the production ratios in the earth can be accounted for by considerations of relative diffusion rates, solubilities, and age of the source rock. Faul et al. (1952) analyzed about 500 helium-bearing natural gas samples for radon, and in all cases found from about 10 to 520 micro-microcuries per liter of natural gas.

The presence of radiogenic $^{4}\text{He}$ and $^{40}\text{Ar}$ has also been detected in many terrestrial samples (Damon and Kulp, 1958a; Funkhauser and Naughton, 1968; Zartman et al., 1961; Stroud et al., 1967; Clarke and Thode, 1964; Wasserburg et al., 1963). Damon and Kulp (1958a) have determined the ratio of excess radiogenic helium to excess radiogenic argon in beryls and cordierites to be between 0.5 and 130, with an average of 20. Zartman et al. (1961) have examined 41 natural gases and found the ratio of helium to radiogenic argon ($^{40}\text{Ar}_{\text{r}}$) to vary between 1.61 and 134, with an average of about 10. Stroud et al. (1967) examined 10 natural gas samples. The $^{4}\text{He}/^{40}\text{Ar}_{\text{r}}$ ratio ranged from 4 to 18, the median being 13. Clarke and Thode (1964) report $^{4}\text{He}$ and $^{40}\text{Ar}_{\text{r}}$ abundances in 4 natural gas samples. The $^{4}\text{He}/^{40}\text{Ar}_{\text{r}}$ ratios range from 9.4 to 20.0. Wasserburg et al. (1963) report
radiogenic helium to radiogenic argon to have ratios ranging from 4 to 13 in 37 natural gas samples.

In addition to the well-documented radiogenic Ar$^{40}$ and He$^{4}$, excesses of He$^{3}$, Ne$^{21}$, Ne$^{22}$ and Ar$^{38}$ have been found in terrestrial samples. Damon and Kulp (1958a) summarize the evidence that atmospheric He$^{3}$ is produced by spallation reactions of primary cosmic rays in the upper atmosphere and by the reaction of secondary neutrons on nitrogen, N$^{14}$(n,$H^{3}$)C$^{12}$. However Aldrich and Nier (1948) found the He$^{3}$ content in natural gas to be about $10^{-7}$ cc STP He$^{3}$ per cc STP He$^{4}$. This is about an order of magnitude smaller than the atmospheric He$^{3}$/He$^{4}$ ratio. Hill (1941) and Morrison and Pine (1955) have suggested that He$^{3}$ in rocks may be produced by neutron capture on lithium, Li$^{6}$(n,$\gamma$)H$^{3}$ → He$^{3}$ + $\beta^{-}$.

Fleming and Thode (1953b) and Wetherill (1954) discovered that minerals rich in uranium or thorium have excess Ne$^{21}$, Ne$^{22}$ and Ar$^{38}$. These have been attributed to nuclear reactions on oxygen, fluorine and chlorine; O$^{18}$($\alpha$,$n$)Ne$^{21}$, F$^{19}$($\alpha$,$p$)Na$^{22}$ → Ne$^{22}$ + $\beta^{-}$, and Cl$^{35}$(\alpha$\gamma$,$p$)Ar$^{38}$. Bogard et al. (1965) confirmed the presence of these same isotopic anomalies in thucholite, a hydrocarbon mineral relatively rich in thorium and uranium. In natural gas samples Emerson et al. (1966) and Stroud et al. (1967) also report an excess of Ne$^{21}$, Ne$^{22}$ and Ar$^{38}$. They report Ar$^{38}$/Ar$^{36}$ ratios ranging from that in the atmosphere, Ar$^{38}$/Ar$^{36}$ = 0.1863 (Nier, 1950a), to an upper value of Ar$^{38}$/Ar$^{36}$ = 0.2007. Stroud et al. (1967) found that the ratio of excess He$^{4}$ to excess Ne$^{21}$ in the natural gases ranges from $2.9 \times 10^{-7}$ to $5.9 \times 10^{-7}$. The narrow range of these values suggests that the excess Ne$^{21}$ is
produced by the nuclear reactions suggested by Fleming and Thode (1953b) and Wetherill (1954).

In addition to anomalies resulting from nuclear reactions in nature, the depletion of certain common radioactivities can produce apparent anomalies. Thus, the report of excess Ar^{36} in volcanic rock samples (Cherdynsev and Shitov, 1967) has been attributed to the trapping of ancient atmospheric gas in material very poor in potassium. The subsequent decay of K^{40} and the leakage of the decay product, Ar^{40}, to the atmosphere results in a lower Ar^{36}/Ar^{40} ratio in the atmosphere than is present in the volcanic rock.

Unlike the light weight noble gases, xenon and krypton appear to have a rather constant isotopic composition in all terrestrial rocks and minerals, except in uranium- and thorium-rich minerals, where fission has produced excess Xe^{131-136} and Kr^{83-86} (Wetherill, 1953; Fleming and Thode, 1953a).

Clarke and Thode (1964) and Wasserburg and Mazor (1964) have found the isotopic composition of krypton in natural gas to be essentially atmospheric. Butler et al. (1963), Clarke and Thode (1964), and Wasserburg and Mazor (1964) have examined xenon in helium rich natural gas and Butler et al. (1963) and Wasserburg and Mazor (1964) have also studied xenon from CO_{2} wells. Except for atmospheric abundances of Xe^{129} in some of Clarke and Thode’s (1964) samples, all these investigations found excess Xe^{129} and Xe^{131-136}. Butler et al. (1963) and Clarke and Thode (1964) found the yields of Xe^{129}, Xe^{131} and Xe^{132} to be above that expected from spontaneous fission of U^{238}. Since Kennett and Thode (1960) and Clarke (1962) reported
large excesses of $\text{Xe}^{131}$ and $\text{Xe}^{132}$ were released in low temperature fractions of xenon from uranium oxides, Clarke and Thode (1964) suggested that low temperature leakage of xenon fission products from the source rock might account for the apparently high yields of $\text{Xe}^{129}$, $\text{Xe}^{131}$ and $\text{Xe}^{132}$ in natural well gas. This mechanism requires that only a very small fraction of the available fission-product xenon has diffused into the natural gas wells, and seems to be incompatible with the high yields of $\text{Xe}^{129}$, $\text{Xe}^{131}$ and $\text{Xe}^{132}$ in CO$_2$ well gas resulting from high temperature decomposition of carbonate rocks by intrusive basalt (Butler et al., 1963).

Regardless of the origin of the excess $\text{Xe}^{129}$, $\text{Xe}^{131}$ and $\text{Xe}^{132}$ in the natural gas wells, it is noteworthy that atmospheric xenon is enriched in these same xenon isotopes relative to primordial xenon in meteorites. Reynolds (1960a, b) first noted this enrichment of heavy xenon isotopes in the atmosphere and suggested that mass fractionation was involved. Kuroda (1960) suggested that fission decay of an extinct transuranium element, such as $\text{Pu}^{244}$, could account for the excess of heavy xenon isotopes in the atmosphere. Both of these hypotheses encountered difficulties; Reynolds' mechanism could not easily account for an abrupt change in the isotopic fractionation pattern at $\text{Xe}^{132}$ and for the absence of isotopic mass fractionation across the lighter noble gases; and Kuroda's hypothesis required very high fission yields at $\text{Xe}^{131}$ and $\text{Xe}^{132}$. Although Butler et al. (1963) and Clarke and Thode (1964) found the yields of $\text{Xe}^{131}$ and $\text{Xe}^{132}$ in well gas to be higher than the yields from spontaneous fission of $\text{U}^{238}$, neither of these investigators report yields of $\text{Xe}^{131}$ and $\text{Xe}^{132}$
which are high enough to produce atmospheric xenon from the primordial xenon seen in meteorites.

The study of noble gases in meteorites has been appreciably more active than the corresponding studies in terrestrial materials. The isotopic abundances of the noble gases in meteorites have been used to calculate the time interval between synthesis of the elements and formation of meteorites, the period of time during which radiogenic helium and argon have been accumulating in the meteorites, and the length of time that the meteorites were exposed to high energy cosmic radiations. For a complete review of the calculations of meteorite ages, see Anders (1962).

Early investigations of noble gases in meteorites revealed only those noble gas isotopes produced by nuclear reactions (Arrol et al., 1942; Gerling and Pavlova, 1951; Reasbeck and Mayne, 1955; Gentler and Zahringer, 1955). The first primordial helium, neon, and argon were found by Gerling and Levskii (1956) in the achondrite meteorite, Staroe Pesyanoe. The actual isotopic composition of heavier noble gases were probably first observed in meteorites by Reynolds (1960a), although earlier investigators (Wasserburg and Hayden, 1955; Reynolds and Lipson, 1956) had reported that the xenon in meteorites was identical to atmospheric xenon. The mass fractionation pattern of these primordial noble gases was similar to that in the earth's atmosphere, except in the heavy mass region where the krypton shows a ten-fold greater separation from xenon than is observed in the atmosphere (Canalas, et al., 1968).

The mass fractionation pattern of noble gases (Canalas et al., 1968) is sufficiently steep to result in significant alteration of
the relative isotopic abundances of the light weight noble gases. For example, Manuel (1967) shows that mass fractionation of neon in the Fayetteville chondrite (Ne$^{20}$:Ne$^{21}$:Ne$^{22} = 12.6:0.033:1.00) could produce atmospheric neon (Ne$^{20}$:Ne$^{21}$:Ne$^{22} = 9.80:0.029:1.00). Krummenacher et al. (1962) suggested that the isotopes of atmospheric xenon may result from very steep fractionation of the xenon in the Murray meteorite (Reynolds, 1960b), but this hypothesis is in conflict with the fact that the Kr/Xe ratio in the atmosphere is ten times larger than the Kr/Xe ratio in Murray.

The small differences in the isotopic composition of krypton isotopes in meteorites relative to the atmosphere appear to fit the pattern expected from mass fractionation (Marti, 1967; Eugster et al., 1967), but the relative enrichment of the heavier krypton isotopes in meteorites makes it appear that meteoritic krypton has been more fractionated than atmospheric krypton. This pattern is opposite to that observed across the neon and xenon isotopes (Reynolds, 1960a, b; Manuel, 1967; Marti, 1967; Eugster et al., 1967).
III. EXPERIMENTAL

A detailed description of the instrument was given by Reynolds (1956), and operation details were given by Canalas (1967). Modifications of the sample system of the mass spectrometer have been made since Mr. Canalas' work. Figure I shows a schematic of the sample system as used during these studies.

The following description of procedure refers to the schematic drawing of the sample system shown as Figure I. Before each analysis titanium furnaces ($A_1$ and $A_2$), copper oxide furnace (B), charcoal finger (F), and tungsten filament (E) are de-gassed at elevated temperature. At the start of an analysis, the copper oxide furnace is brought to 550°C with valves V-1 and V-2 open. The valve V-1 is then closed and the break-off tip of a gas or air spike (C) is broken by a glass encased metal slug. Any hydrocarbons in the gas are oxidized to $CO_2$ and $H_2O$ on the copper oxide at 550°C. After 15-30 minute, depending on sample size, the titanium furnace $A_1$ is brought to 850°C and maintained at this temperature for 20 minutes, with the copper oxide furnace maintained at 550°C. Then both the titanium and copper oxide furnaces are cooled by compressed air.

After the furnaces are cool, crushed dry ice is placed on trap 1, valve V-2 is closed, and liquid nitrogen is placed on the charcoal finger. After 5 minutes valve V-1 is opened, and gases
are absorbed on the charcoal finger for 15 minutes. Valve V-1 is then closed and the second titanium furnace (A2) is brought up to 850°C. A resistance heater now replaces liquid nitrogen on the charcoal finger to drive off absorbed gases, and the tungsten filament is heated to pale yellow heat to "crack" unreacted hydrocarbons. This enables the titanium getter to scrub out the remaining unreacted gases in 20 minutes. The titanium furnace is then cooled by air blast, and the tungsten filament and charcoal heater are maintained hot until the titanium cools. The tungsten filament is then turned off and allowed to cool.

At this point dry ice is placed on trap 2 and after 5 minutes, liquid nitrogen replaces the heater on the charcoal. After a one hour equilibration period, the mass spectrometer is closed from pumping and the helium and neon are admitted through valve V-3. Since He³ and neon are only present in trace amounts, these are determined in this first fraction of helium and neon. The He⁴ in natural gas is too abundant for detection during analysis of this first fraction. To determine He⁴ the concentration of He⁴ is reduced by successive expansion of the helium from the sample system into the spectrometer. One expansion involves pumping the gases from the mass spectrometer through a separate valve not shown in figure I, closing this valve, and admitting the next gas fraction into the mass spectrometer through valve V-3. This cycle is repeated until the He⁴ signal is small enough to be measured. After analyzing He⁴ one additional expansion is performed to measure the fraction of helium which enters the spectrometer with each expansion.
By this time the concentration of He\(^4\) remaining in the sample system is small enough that it will not interfere with the argon analysis, and it is not pumped from the sample side before the argon analysis. After the last He\(^4\) fraction is admitted into the mass spectrometer, the liquid nitrogen on the charcoal finger is replaced by Dry Ice-isopropanol (-78°C) to release argon. During a one hour time interval allowed for equilibration of gases on the charcoal at -78°C, the last He\(^4\) fraction is pumped from the mass spectrometer.

Because there is so much radiogenic Ar\(^{40}\) in the natural gas samples, the argon must be analyzed in two fractions as follows:

1) The mass spectrometer is focused on mass 40, closed from pumping, and valve V-3 is partially opened until the amount of Ar\(^{40}\) in the spectrometer approaches the upper limit of detectability. The valve V-3 is then closed and this first argon fraction is statically analyzed. The first argon fraction is then pumped from the mass spectrometer. 2) The mass spectrometer is again closed from pumping, but the mass spectrometer is focused on mass 36. The second argon fraction is admitted into the mass spectrometer with valve V-3 open wide. After valve V-3 is closed, the Ar\(^{36}\) and Ar\(^{38}\) in this second argon fraction are measured, and then the argon is pumped from the mass spectrometer. The residual argon is pumped from the sample side by opening valve V-2 for five minutes.

The procedure for krypton and xenon is more simple since the total amounts of these two gases can be detected without dividing either gas into fractions. Mercury at its freezing point (-39°C) is maintained on the charcoal finger for one hour to release krypton.
This is admitted into the mass spectrometer and scanned, then pumped from the spectrometer. The residual krypton in the sample side does not interfere with xenon analysis and is not pumped out. During krypton analysis, the charcoal finger is heated to 200°C to drive off all the remaining adsorbed gases. After at least 20 minutes of equilibration, this xenon fraction is admitted into the mass spectrometer and scanned.

This procedure of gas analysis produces a record in chart form. Each isotope of each noble gas is "swept" from 6 to 10 times, and the peak heights and base line for each different detection scale are visually measured with a linear scale marked with 50 divisions per inch. The raw data are then reduced by computer.

The natural gases analyzed in this study were collected in pressurized containers which had been flushed with the gas prior to collection. In order to prevent any fractionation of the gases when filling small volume spikes for analysis, the original containers were connected to a spike filling system through two teflon-seal stopcocks separated by a small reservoir. The volume of this reservoir was such that gas filling pressures of about 6-9 torr resulted from the expansion of this reservoir into the total volume of the spike-filling system. Calibrated spikes with break-seals were attached to the system, the system was pumped to $10^{-5}$ mm Hg, flushed with a volume of gas from the reservoir, and evacuated to $10^{-7}$ torr. The system was then closed from pumping and one spike sealed at this pressure to be analyzed as a system blank.
The small reservoir between the two stopcocks was then filled and expanded into the spike filling system. Spikes of about 1-30 cm³ were then sealed off at pressures of about 6-9 mm Hg, and these spikes were connected to the sample system of the mass spectrometer.

A total of eight such volumes of natural gas were analyzed using a single titanium getter. Due to the appearance of hydrocarbon peaks in the mass spectrometer when these samples were analyzed, the entire data were discarded. After modifying the sample system by connecting an additional titanium furnace, a copper oxide furnace, and a tungsten filament, the analyses described in this thesis were performed.

Relevant data on the four natural gas samples reported in this work are given in Table I. It should be noted that sample C-16 is a "plant residue" gas supplied by Union Oil Company, a subsidiary of Pure Oil Company, and the listed additional analyses relate to a single gas well in this immediate area owned by Pure Oil Company. Zartman et al. (1961) have analyzed a gas sample from the same well from which sample B-62 was obtained, Sleeper unit #1, owned by Shell Oil Company. Samples C-17 and B-69 were provided by the Bureau of Mines, and are presumed to have been collected in early 1968 or late 1967. Samples C-17, B-69 and B-62 are from the Panhandle area of Texas and Oklahoma, and sample C-16 is from Utah.
IV. RESULTS AND DISCUSSION

A. Abundance Pattern

The concentration of $\text{He}^4$ and a standard nonradiogenic isotope of each of the other noble gases are shown in Table II. The concentrations of noble gases in the atmosphere are shown for comparison. Relative to the atmosphere there is a depletion of xenon in the natural gas samples by about a factor of 10 and a generally increasing depletion of the lighter weight noble gases, except for the radiogenic $\text{He}^4$. Since lighter weight noble gases would be expected to preferentially leak from the earth, the abundance pattern of gases presently leaking from the earth is expected to show a steeper mass fractionation pattern than is observed in the gases which have earlier escaped to the atmosphere. Thus, the abundance pattern of noble gases shown in Table II qualitatively appears to support our earlier suggestion that the radiogenic $\text{He}^4$ and $\text{Ar}^{40}$ in natural gas wells are accompanied by other noble gases whose isotopic composition may reflect the direction of change of atmospheric noble gases. Clarke and Thode (1964) and Wasserburg and Mazor (1964) have earlier reported an enrichment of the heavier noble gases in helium-bearing natural gas samples.

In order to quantitatively compare the abundance pattern of the noble gases in natural gas with the abundance pattern observed in other samples, Canalas et al. (1968) have defined a fractionation factor, $F_m$, relative to the heaviest non-radiogenic xenon isotope:
In equation 1 the term $X^m$ is any noble gas isotope of mass number $m$, and the ratio $(X^m/Xe^{130})_{\text{cosmic}}$ is from the cosmic abundances given by Suess and Urey (1956). The fractionation factors for noble gases in the atmosphere, the natural gas samples, and the Murray meteorite are shown in Table III and in Figure II. The noble gas data on Murray meteorite was chosen for comparison because it is reported to contain more xenon than any other meteorite, except Novo Urei, and all of the noble gases in the Murray meteorite have been measured on a single sample (Reynolds, 1960b).

As can be seen in Figure II, there is a greater separation of argon and krypton from xenon in the natural gas samples than in the atmosphere, but less separation than in the Murray chondrite. The argon and krypton depletions are well correlated for these samples, and the same general correlation is observed for neon, except for sample C-17 which has almost exactly an order of magnitude greater depletion of neon from argon than do the other natural gas samples. Since He$^4$ is radiogenic, its abundance relative to xenon does not reflect the mass fractionation seen across the other noble gases. However, in general those samples which exhibit the more atmosphere-like fractionation pattern of krypton and argon (B-69 and C-17) also exhibit more nearly the atmospheric fractionation for helium.

This correlation of fraction patterns for noble gases from such diverse sources suggests that an atmospheric component may be present in varying degrees in these natural gas samples. Thus the abundances of noble gases shown in Table II appear to support our earlier
suggestion that the radiogenic He$^4$ and Ar$^{40}$ in these natural gases are accompanied by other noble gases whose isotopic composition may reflect the direction of change of atmospheric noble gases.

B. Helium, Neon and Argon

The isotopic composition of helium, neon and argon is shown in Table IV. The He$^3$/He$^4$ ratios are only approximations calculated from the peak height of He$^3$ when the first fraction of helium was in the mass spectrometer and from the peak height of He$^4$ in the fourth or fifth helium fraction. As noted earlier, the signal of He$^4$ was too large to be detected until the volume of helium had been reduced by successively expanding the gas volume into the mass spectrometer four or five times. Since this procedure was not used on our air spike standards, there was no calibration of the mass spectrometer for the method used to estimate our He$^3$/He$^4$ ratios. Hence the much lower He$^3$/He$^4$ ratios reported to be in natural gas wells by Aldrich and Nier (1948) are probably more accurate than our He$^3$/He$^4$ values in Table 4.

Because of the contribution of doubly ionized Ar$^{40}$ to the mass spectrometer's signal at mass 20, we were not able to accurately measure the concentrations of Ne$^{20}$. The Ne$^{21}$/Ne$^{22}$ ratios in all of our gas samples are higher than the atmospheric Ne$^{21}$/Ne$^{22}$ ratio, presumably due to the $^18$O$(\alpha,n)$Ne$^{21}$ reaction (Wetherill, 1954). The Ar$^{38}$/Ar$^{36}$ values are also slightly higher than the Ar$^{38}$/Ar$^{36}$ ratio in the atmosphere. Such an enrichment of Ar$^{38}$ in radioactive minerals was reported by Fleming and Thode (1953) and attributed to nuclear reactions such as Cl$^{35}$(α,p)Ar$^{38}$. 
The amounts of excess Ne$_{21}$, He$^4$ and Ar$^{40}$ and the ratios of these excesses are shown at the bottom of Table IV. It was assumed that all of the He$^4$ was radiogenic and the excess Ne$_{21}$ and Ar$^{40}$ were calculated by the following equations.

\[(2a) \quad \left[ Ne_{21r} \right] = \left( \frac{Ne_{21}}{Ne_{22}} \right)_{sample} - \left( \frac{Ne_{21}}{Ne_{22}} \right)_{air} \left[ Ne_{22} \right]_{sample} \]

\[(2b) \quad \left[ Ar^{40r} \right] = \left( \frac{Ar^{40}}{Ar^{36}} \right)_{sample} - \left( \frac{Ar^{40}}{Ar^{36}} \right)_{air} \left[ Ar^{36} \right]_{sample} \]

As can be seen in Table IV, the ratios of He$^4$/Ar$^{40}$ and He$^4$/Ne$_{21r}$ are in good agreement with the values reported in other gas wells by Stroud et al. (1967). It would be noted that Stroud et al. (1967) concentrated neon from approximately $10^4$ to $10^6$ times the volume of natural gas of the largest sample in this study. The He$^4$/Ar$^{40}$ ratios are also in general agreement with earlier work of Wasserburg et al. (1957), Zartman et al. (1961) and Wasserburg et al. (1963). Zartman et al. (1961) have shown that the present production ratio of radiogenic helium to radiogenic argon in average igneous rocks and in a wide variety of sediments is He$^4$/Ar$^{40} \approx 7$. They have also shown that this production ratio would decrease to He$^4$/Ar$^{40} \approx 2$ about 4.5 billion years ago, and the production ratio in chondritic material would vary from about 1 for modern chondrites to about 0.3 some 4.5 billion years ago.

Since the preferential escape of radiogenic He$^4$ over Ar$^{40}$ from rocks and minerals is well documented (Kirsten et al., 1962; Kirsten et al., 1968) it seems unlikely that the He$^4$/Ar$^{40}$ ratio in natural gas samples would be lower than the production ratios in the source rock. For this reason we would not interpret the He$^4$/Ar$^{40}$ ratios in Table IV as evidence that these gases were derived exclusively from degassing of igneous or sedimentary material.
Before ending the discussion of these light weight noble gases, it should be noted that the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, the $^{21}\text{Ne}/^{22}\text{Ne}$ ratios, and the $^{3}{\text{He}}/^{4}\text{He}$ ratios in Table IV show a general trend of approaching the atmospheric values as the fractionation patterns in Figure II approach the fractionation pattern of atmospheric gases. Since atmospheric contamination cannot be completely prevented, we believe that the isotopic composition of noble gases in C-16 best represents the direction of change of noble gases in the atmosphere as the degassing of the earth continues, and that the likelihood of an atmospheric component in these natural gases increases in going from C-16 to B-62 to C-17 to B-69.

C. Xenon and Krypton

Within experimental error, all of the natural gas samples analyzed in this work appeared to contain krypton of atmospheric composition. This agrees with earlier work of Clarke and Thode (1964) and Wasserburg and Mazor (1965). These authors note that any fission component would be more difficult to detect in krypton than in xenon because of the higher concentrations of krypton and the lower fission yields in the krypton mass region than in the xenon mass region.

The isotopic composition of xenon in the natural gas samples is shown in Table V with the isotopic composition of xenon from the atmosphere and from the Novo Urei meteorite. The xenon from Novo Urei was chosen for comparison because it has the highest xenon content of any meteorite reported to date (Marti, 1967) and this is the only meteorite which has a $^{129}\text{Xe}/^{130}\text{Xe}$ ratio lower than that in
the atmosphere. The concentrations of Xe$^{124}$ and Xe$^{126}$ were too low to be measured in the smaller gas samples, B-69 and B-62, and were near the detection limit in C-17 and C-16. The values of Xe$^{124}$ and Xe$^{126}$ for C-17 may therefore contain relatively large errors in addition to the statistical errors shown in Table V. Due to previous analyses of neutron-irradiated samples containing a large excess of Xe$^{128}$, the mass spectrometer had an unusually large Xe$^{128}$ "memory" peak. For this reason no values for Xe$^{128}$ are shown for samples B-69 and B-62, and the values from C-17 and C-16 should only be considered as upper limits. Because of the uncertainties in the three lightest xenon isotopes, we will not discuss the differences in the Xe$^{124}$, Xe$^{126}$ and Xe$^{128}$ values shown in Table V, except to note that the abundance of these three isotopes in natural gas relative to Xe$^{130}$ are intermediate between the values in the atmosphere and in the Novo Urei meteorite.

The heavy xenon isotopes, Xe$^{129}$ and Xe$^{131-136}$, appear to be enriched in all of these natural gas samples relative to xenon in the atmosphere. Other investigators have observed an enrichment of the heavy xenon isotopes in He-rich natural gas and in CO$_2$-well gas (Butler et al., 1963; Clarke and Thode, 1964; Wasserburg and Mazor, 1965) Although all of these investigators suggest that the enrichment of heavy xenon isotopes results from spontaneous fission, Clarke and Thode (1964) and Butler et al. (1963) found the yields of Xe$^{129}$, Xe$^{131}$ and Xe$^{132}$ to be higher than expected from the spontaneous fission of U$^{238}$.

Since the xenon in the atmosphere also shows an unusually high yield at Xe$^{131}$ and Xe$^{132}$ (Kuroda, 1960; Krummenacher et al., 1962)
it appears that the xenon in natural gas may result from one or both of the two mechanisms proposed to explain these atmospheric anomalies. In order to consider the mass fractionation mechanism proposed by Reynolds (1960a) and explained in detail by Krummenacher et al. (1962), the per mil excess of each of the heavy xenon isotopes in natural gas samples has been calculated relative to the atmosphere,

\[ \delta^i = \left[ \frac{(Xe^i/Xe^{130})_{\text{sample}}}{(Xe^i/Xe^{130})_{\text{air}}} - 1 \right] \times 1000 \]

and relative to the Novo Urei meteorite.

\[ \delta^i = \left[ \frac{(Xe^i/Xe^{130})_{\text{sample}}}{(Xe^i/Xe^{130})_{\text{Novo Urei}}} - 1 \right] \times 1000 \]

To consider the excess heavy xenon isotopes as fission products (Kuroda, 1960), the following equations are useful.

\[ \Delta^i = (Xe^i/Xe^{130})_{\text{sample}} - (Xe^i/Xe^{130})_{\text{air}} \]

\[ \Delta^i = (Xe^i/Xe^{130})_{\text{sample}} - (Xe^i/Xe^{130})_{\text{Novo Urei}} \]

The results from equation (3) and equation (4) are shown in Table VI, and in Figures III-VI.

The data in Table VI and in Figures III-VI show a close correlation of the excess \( Xe^{129}, Xe^{131}, Xe^{132}, Xe^{134} \) and \( Xe^{136} \) in these four natural gas samples. In comparing meteoritic and atmospheric xenon, Reynolds (1960a) showed that a plot of the per mil \( \delta^i \) values from equation (3a) versus the square-root of the mass number fit a straight line for the isotopes lighter than \( Xe^{134} \). He and Krummenacher et al. (1962) suggested that this pattern results from mass fractionation. A similar plot of the xenon from natural gas wells is shown in Figure III together with the xenon from Novo Urei (Marti, 1967). As can be seen in Figure III, the per mil excess of the heavy xenon isotopes from the well gases do not appear to fit a
straight line as expected from fractionation of atmospheric xenon. In Figure IV the per mil excess of heavy xenon isotopes relative to xenon in Novo Urei is shown. Although the Xe\(^{130}\), Xe\(^{131}\) and Xe\(^{132}\) points fit a straight line, the correlations of excess Xe\(^{131}\) and Xe\(^{132}\) with the excess Xe\(^{129}\), and with the excess Xe\(^{134}\) and Xe\(^{136}\) in both atmospheric and natural gas xenon seems to rule out simple mass fractionation as a mechanism to explain the discrepancies between meteoritic and atmospheric xenon.

The alternate hypothesis put forth by Kuroda (1960) is that the enrichment of heavy xenon isotopes in the atmosphere results from fission. To test this hypothesis we use equation (4a) to calculate the fission yield of heavy xenon isotopes in natural gas relative to atmospheric xenon. The results shown in Figure V indicate that the "fission yields" pattern of xenon in natural gas is almost the mirror image of the depletion pattern of these same xenon isotopes in Novo Urei, and the very high yields at Xe\(^{129}\), Xe\(^{131}\) and Xe\(^{132}\) are unlike any known fission pattern (Kuroda, 1960). Butler et al. (1963) have observed unusually high yields of Xe\(^{129}\), Xe\(^{131}\) and Xe\(^{132}\) in a CO\(_2\)-well gas, and Clarke and Thode (1964) report abnormally high yields of Xe\(^{131}\) and Xe\(^{132}\) in helium-bearing natural gas.

When the "fission yield" pattern of heavy xenon isotopes in the atmosphere and in natural gas are calculated relative to Novo Urei (equation (4b)), the resemblance of the "fission" pattern in the atmosphere and in the natural gas samples is remarkable. This is shown in Figure VI. In spite of the relatively large statistical errors on our \(\Delta^1\) values, we believe that (1) the consistent pattern
of the heavy xenon isotopes in natural gas, (2) the resemblance to the pattern of heavy xenon isotopes in the atmosphere, and (3) the earlier reports of unusually high yields of Xe$^{129}$, Xe$^{131}$ and Xe$^{132}$ in gas wells, all point to a common source for the heavy xenon in the atmosphere and in gas wells. Since these five xenon isotopes, Xe$^{129}$, Xe$^{131}$, Xe$^{132}$, Xe$^{134}$ and Xe$^{136}$, are the only xenon isotopes not shielded from $\beta$-decay by a stable neutron-rich isobar, the fission hypothesis of Kuroda (1960) seems to be the most feasible mechanism for the production of these xenon isotopes.

In order to compare the fission yields in our natural gas samples with the fission component in the atmosphere and in other gas wells, we employ in Figure VII the xenon isotope correlation plot used by Funk et al. (1967) to estimate the fission yields of xenon in meteorites. This plot is useful in that any mixture of two components must lie on the line connecting these components, or any mixture of three or more components must lie within the area bounded by lines connecting these components. On such a plot the xenon released at 600°C from Renazzo (Reynolds and Turner, 1964) and from a total melt of Bjurbøle matrix (Alexander and Manuel, 1969) appear to have the smallest component of atmospheric or fissionogenic xenon. The xenon from these two meteorites is therefore used to estimate "primordial" xenon.

As would be expected from the correlations seen in Figure VI, the xenon which we measured in natural gas samples lies very close to an extension of the solid line connecting "primordial" and atmospheric xenon in Figure VII. Thus a mixture of "primordial" xenon with the $\beta$-unshielded xenon isotoped enriched in our gas samples
could produce the atmospheric abundance pattern of xenon isotopes heavier than Xe\textsuperscript{128}. Since the dashed line in Figure VII extrapolate to the spontaneous fission yields of U\textsuperscript{238} (Young and Thode, 1960), the trapped xenon in any gas sample containing a fission component from U\textsuperscript{238} would lie on the dashed line to the left of the total xenon in the gas sample. Thus the xenon in gas wells analyzed by Butler et al. (1963) and by Clarke and Thode (1964) could result from a mixture of U\textsuperscript{238} fissionogenic xenon with xenon as seen in the natural gas wells reported here.

Near the top of Figure VII is a line connecting "primordial" and fission produced xenon as reported in the Pasamonte meteorite (Rowe and Kuroda, 1965; Hohenberg et al., 1967). From a series of heating experiments on Pasamonte, Hohenberg et al. (1967) have convincing evidence that this fission pattern results from the decay of extinct Pu\textsuperscript{244}. Although not shown in Figure 7, a line connecting atmospheric and Pasamonte-type fission xenon would lie very close to the xenon in gas wells reported by Butler et al. (1963) and Clarke and Thode (1964). Thus, a mixture of atmospheric and Pasamonte-type xenon is an alternate explanation for their data.

The parent nuclide capable of producing the fission yield pattern shown in Figure VI and Figure VII can only be surmised. The sharp maximum at mass 132 and the almost equal yields of Xe\textsuperscript{129}, Xe\textsuperscript{131}, Xe\textsuperscript{134} and Xe\textsuperscript{136} are unlike any known fission yield pattern. However, Kuroda (1960) has pointed out that the spontaneous fission yields of both U\textsuperscript{238} and Cm\textsuperscript{242} display a fine structure maximum at mass 132. If the fine structure fission yields of U\textsuperscript{235} at mass 134 arise from
closed shell effects at 82 neutrons in Te$^{134}$ (Glendenin, 1949; Pappas, 1953), then it seems that the more neutron rich transuranium elements might be capable of producing a fine structure such as that in Figure VI due to the doubly magic Sn$^{132}$.

Even is one accepts that the high fission yield for Xe$^{132}$ is feasible, the almost equal yields of Xe$^{129}$, Xe$^{131}$, Xe$^{134}$ and Xe$^{136}$ shown in Figure VI remain as an apparently valid objection to the fission hypothesis. The only region where such nearly equal yields might be encountered is atop one of the two broad mass-yield curve maxima of asymmetric fission or near one-half the mass of the parent nuclide for symmetric fission. Hyde (1960) notes that in the asymmetric fission of elements below thorium the heavy-fragment "wing" remains fixed and the light-fragment "wing" shifts to compensate for the lighter fissioning elements. Thus it does not seem likely that the fission yield pattern of xenon isotopes in natural gas and in the atmosphere can be assigned to the heavy-fragment "wings" of some nuclide lighter than thorium or uranium.

The alternate possibility, that the xenon isotopes result from symmetric fission, is not supported by any experimental evidence of a symmetric mode of spontaneous fission for the transuranium elements near mass 270. The heaviest nuclide on which accurate fission yields of xenon have been reported, Cf$^{252}$, shows a fission pattern similar to that from the spontaneous fission of U$^{238}$ except for a higher yield of Xe$^{131}$ from Cf$^{252}$ than from U$^{238}$ (Srinivasan et al., 1969). However Hyde (1960) notes that the symmetric mode of fission observed in the lead-bismuth region may be related to
the closed shell effect of 82 protons and 126 neutrons. As the mass number increases or decreases from the lead-bismuth region the nuclei become stabilized in a deformed shape and asymmetric fission appears. If one assumes that a heavy transuranium element near mass number 270 is to survive from the time of nucleosynthesis until the formation of the earth, then the relatively short half-lives observed in the nuclei with mass number greater than 250 suggests that some closed shell stabilizing effect would be required if the trend toward shorter half-lives is to be reversed in the 270 mass region. It therefore does not seem unreasonable that symmetric fission of a long-lived transuranium nuclide could be responsible for the fission yields observed across the xenon isotopes in natural gas wells.
V. CONCLUSIONS

The results of this investigation may be summarized as follows:

(1) The fractionation pattern of noble gases in natural well gases was found to increase with well depth. The greatest isotopic anomalies of noble gases were also observed in the deepest wells.

(2) The values of radiogenic He$_4$/Ne$^{21}$ in these gas samples were in good agreement with the values observed in other natural gases by Stroud et al. (1967). The absence of large variations in the He$_4$/Ne$^{21}$ ratio is interpreted as additional evidence that the Ne$^{21}$ arises from nuclear reactions associated with $\gamma$-activity (Wetherill, 1954).

(3) The radiogenic He$_4$/Ar$^{40}$ ratios in these gas samples were in good agreement with the values reported in other well gas samples (Zartman et al., 1961; Wasserburg et al., 1963; Clarke and Thode, 1964; Stroud et al., 1967).

(4) No isotopic anomalies of krypton were observed. This agrees with the work of Clarke and Thode (1964) and Wasserburg and Mazor (1965).

(5) Our analyses confirmed the presence of unusually high yields of Xe$^{129}$, Xe$^{131}$ and Xe$^{132}$ in well gases (Butler et al., 1963; Clarke and Thode, 1964). However we also found a consistent correlation of the excess Xe$^{129}$, Xe$^{131}$ and Xe$^{132}$ with excess Xe$^{134}$ and Xe$^{136}$. The pattern of these excess xenon isotopes in well gases is such that the addition of these isotopes to primordial xenon seen in the
Novo Urei meteorite could produce the abundance pattern of all atmospheric xenon isotopes heavier than Xe$^{128}$. It is suggested that symmetric fission of a long-lived nuclide in the 270 mass region could produce the observed pattern of excesses for all of the non-$\beta$-shielded xenon isotopes.

(6) The presence of such high yields of Xe$^{129}$ from fission suggests that the large Xe$^{129}$ anomaly in meteorites (Reynolds, 1960a) could result from the preferential retention of the mass 129 fission product in the meteorites due to the 17-million year $\lambda^{129}$ precursor.
<table>
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<tr>
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<th>C-16</th>
<th>C-17</th>
<th>B-69</th>
<th>B-62</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume of sample (cc/STP)</strong></td>
<td>0.2476</td>
<td>0.1955</td>
<td>0.03569</td>
<td>0.03783</td>
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<tr>
<td><strong>Sample taken</strong></td>
<td>April, 1968</td>
<td>unknown</td>
<td>unknown</td>
<td>April, 1968</td>
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**ADDITIONAL ANALYSIS**

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<td>Index Number</td>
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<td>162</td>
<td>-----</td>
<td>703</td>
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<tr>
<td>State</td>
<td>Utah</td>
<td>Texas</td>
<td>Texas</td>
<td>Oklahoma</td>
</tr>
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<td>San Juan</td>
<td>Potter</td>
<td>Potter</td>
<td>Cimmeron</td>
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<tr>
<td>Field</td>
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<td>Cliffside</td>
<td>-----</td>
<td>Keyes</td>
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<td>Well name</td>
<td>N.W. Lisbon USA No. 1</td>
<td>Bivins A-3R</td>
<td>Bush B-3R</td>
<td>Sleeper Unit #1</td>
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<td>Location</td>
<td>Sec. 10-30S-24E</td>
<td>Sec. 26, BKLM 19</td>
<td>Sec. 29, BKLM-19</td>
<td>Sec. 35-6N-9E</td>
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<td>Sampled</td>
<td>1959</td>
<td>1963</td>
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<td>1954</td>
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<td>Red-Cave</td>
<td>Pennsylvanian-Keyes Sandstone</td>
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TABLE I CONTINUED.

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<th>C-17</th>
<th>B-69</th>
<th>B-62</th>
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<tr>
<td>Depth (ft)</td>
<td>8000-9000</td>
<td>2555</td>
<td>2523</td>
<td>4500</td>
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<td>Wellhead pressure (lps)</td>
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<td>482</td>
<td>554</td>
<td>835</td>
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<tr>
<td>Selected components (% by volume)</td>
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<td></td>
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<td>N$_2$</td>
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<td>25.4</td>
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<td>O$_2$</td>
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<td>Trace</td>
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<td>H$_2$</td>
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<td>CO$_2$</td>
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<td>----</td>
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<td>Ar</td>
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<td>Trace</td>
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*Data is on a well in the immediate vicinity of the processing plant at which sample C-16 was obtained*
TABLE II.
CONCENTRATIONS OF NOBLE GASES IN NATURAL GAS
(cc STP/cc STP Natural Gas)

<table>
<thead>
<tr>
<th></th>
<th>Air Nier (1950b)</th>
<th>B-69</th>
<th>C-17</th>
<th>B-62</th>
<th>C-16</th>
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<tbody>
<tr>
<td>He$^4 \times 10^{-6}$</td>
<td>5.24</td>
<td>1000</td>
<td>3920</td>
<td>6350</td>
<td>2220</td>
</tr>
<tr>
<td>Ne$^{22} \times 10^{-9}$</td>
<td>1680</td>
<td>55.0</td>
<td>4.46</td>
<td>12.2</td>
<td>3.93</td>
</tr>
<tr>
<td>Ar$^{36} \times 10^{-7}$</td>
<td>315</td>
<td>25.6</td>
<td>8.26</td>
<td>6.64</td>
<td>1.12</td>
</tr>
<tr>
<td>Kr$^{84} \times 10^{-9}$</td>
<td>650</td>
<td>47.7</td>
<td>38.7</td>
<td>29.9</td>
<td>9.23</td>
</tr>
<tr>
<td>Xe$^{130} \times 10^{-10}$</td>
<td>35.5</td>
<td>3.31</td>
<td>3.29</td>
<td>3.50</td>
<td>1.42</td>
</tr>
<tr>
<td>Volume Analyzed (cc STP)</td>
<td>----</td>
<td>0.03569</td>
<td>0.1955</td>
<td>0.03783</td>
<td>0.2476</td>
</tr>
</tbody>
</table>
TABLE III.

FRACTIONATION FACTOR \( (F^m) \) FOR NOBLE GASES IN THE ATMOSPHERE, IN NATURAL GASES, AND IN THE MURRAY METEORITE

<table>
<thead>
<tr>
<th></th>
<th>( x_m = Hg \times 10^{-3} )</th>
<th>( x_m = Ne^{22} \times 10^{-7} )</th>
<th>( x_m = Ar^{36} \times 10^{-5} )</th>
<th>( x_m = Kr^{84} \times 10^{-1} )</th>
<th>( x_m = Xe^{130} )</th>
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<tr>
<td>Atmosphere</td>
<td>7.775</td>
<td>875</td>
<td>1140</td>
<td>10.0</td>
<td>( \equiv 1.000 )</td>
</tr>
<tr>
<td>B-69</td>
<td>15,820</td>
<td>306</td>
<td>994</td>
<td>7.98</td>
<td>( \equiv 1.000 )</td>
</tr>
<tr>
<td>C-17</td>
<td>62,700</td>
<td>27.9</td>
<td>323</td>
<td>6.51</td>
<td>( \equiv 1.000 )</td>
</tr>
<tr>
<td>B-62</td>
<td>95,400</td>
<td>67.2</td>
<td>245</td>
<td>4.73</td>
<td>( \equiv 1.000 )</td>
</tr>
<tr>
<td>C-16</td>
<td>81,400</td>
<td>53.6</td>
<td>102</td>
<td>3.59</td>
<td>( \equiv 1.000 )</td>
</tr>
<tr>
<td>Murray Reynolds (1960b)</td>
<td>456</td>
<td>100</td>
<td>56.1</td>
<td>0.490</td>
<td>( \equiv 1.000 )</td>
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<tr>
<td></td>
<td>Air</td>
<td>B-69</td>
<td>C-17</td>
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<td>------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
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<tr>
<td>He³/He⁴</td>
<td>1.3 × 10⁻⁶</td>
<td>3.2 × 10⁻⁶</td>
<td>7.4 × 10⁻⁶</td>
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<td>9.4 × 10⁻⁶</td>
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<tr>
<td>Ne²¹/Ne²²</td>
<td>0.02904</td>
<td>0.03050 ±</td>
<td>0.03956 ±</td>
<td>0.04888 ±</td>
<td>---</td>
</tr>
<tr>
<td>Ar³⁸/Ar³⁶</td>
<td>0.1869</td>
<td>0.1878 ±</td>
<td>0.1938 ±</td>
<td>0.1903 ±</td>
<td>0.2055 ±</td>
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<tr>
<td>Ar⁴⁰/Ar³⁶</td>
<td>295.5</td>
<td>474 ± 2</td>
<td>1268 ± 3</td>
<td>2265 ± 38</td>
<td>4990 ± 60</td>
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<tr>
<td>He⁴r (cc/cc)</td>
<td>---</td>
<td>1.00 × 10⁻³</td>
<td>3.92 × 10⁻³</td>
<td>6.35 × 10⁻³</td>
<td>2.22 × 10⁻³</td>
</tr>
<tr>
<td>Ne²¹r (cc/cc)</td>
<td>---</td>
<td>2.53 × 10⁻¹¹</td>
<td>4.69 × 10⁻¹¹</td>
<td>24.2 × 10⁻¹¹</td>
<td>---</td>
</tr>
<tr>
<td>Ar⁴⁰r (cc/cc)</td>
<td>---</td>
<td>4.56 × 10⁻⁴</td>
<td>8.03 × 10⁻⁴</td>
<td>13.0 × 10⁻⁴</td>
<td>5.26 × 10⁻⁴</td>
</tr>
<tr>
<td>He⁴r/Ne²¹r</td>
<td>---</td>
<td>3.95 × 10⁷</td>
<td>8.34 × 10⁷</td>
<td>2.62 × 10⁷</td>
<td>---</td>
</tr>
<tr>
<td>He⁴r/Ar⁴⁰r</td>
<td>---</td>
<td>2.29</td>
<td>4.88</td>
<td>4.88</td>
<td>4.22</td>
</tr>
</tbody>
</table>

¹All of the data on other gas wells are from Stroud, Meyer and Emerson (1967), except the He³/He⁴ ratios which are from Aldrich and Nier (1948).
### TABLE V.

**ISOTOPIC COMPOSITION OF XENON IN NATURAL GAS, AIR AND THE NOVO UREI METEORITE**  
\((\text{Xe}^{130} = 1.000)\)

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Air Nier (1950b)</th>
<th>B-69</th>
<th>C-17</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>0.02353</td>
<td>-----</td>
<td>0.02385 ± 0.00050</td>
</tr>
<tr>
<td>126</td>
<td>0.02206</td>
<td>-----</td>
<td>0.02291 ± 0.00067</td>
</tr>
<tr>
<td>128</td>
<td>0.4703</td>
<td>-----</td>
<td>0.4750 ± 0.0120</td>
</tr>
<tr>
<td>129</td>
<td>6.480</td>
<td>6.489 ± 0.037</td>
<td>6.504 ± 0.038</td>
</tr>
<tr>
<td>130</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>131</td>
<td>5.191</td>
<td>5.228 ± 0.021</td>
<td>5.247 ± 0.031</td>
</tr>
<tr>
<td>132</td>
<td>6.591</td>
<td>6.636 ± 0.026</td>
<td>6.661 ± 0.026</td>
</tr>
<tr>
<td>134</td>
<td>2.559</td>
<td>2.572 ± 0.005</td>
<td>2.614 ± 0.009</td>
</tr>
<tr>
<td>136</td>
<td>2.174</td>
<td>2.213 ± 0.004</td>
<td>2.241 ± 0.008</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>B-62</th>
<th>C-16</th>
<th>Novo Ureii Marti (1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>-----</td>
<td>0.02688 ± 0.00054</td>
<td>0.02805 ± 0.00093</td>
</tr>
<tr>
<td>126</td>
<td>-----</td>
<td>0.02589 ± 0.00065</td>
<td>0.02533 ± 0.00062</td>
</tr>
<tr>
<td>128</td>
<td>-----</td>
<td>0.4920 ± 0.0120</td>
<td>0.5006 ± 0.0050</td>
</tr>
<tr>
<td>129</td>
<td>6.535 ± 0.049</td>
<td>6.672 ± 0.113</td>
<td>6.340 ± 0.037</td>
</tr>
<tr>
<td>130</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>131</td>
<td>5.248 ± 0.030</td>
<td>5.427 ± 0.052</td>
<td>5.045 ± 0.025</td>
</tr>
<tr>
<td>132</td>
<td>6.684 ± 0.032</td>
<td>6.914 ± 0.088</td>
<td>6.195 ± 0.062</td>
</tr>
<tr>
<td>134</td>
<td>2.632 ± 0.007</td>
<td>2.746 ± 0.021</td>
<td>2.362 ± 0.019</td>
</tr>
<tr>
<td>136</td>
<td>2.249 ± 0.012</td>
<td>2.381 ± 0.017</td>
<td>1.982 ± 0.019</td>
</tr>
</tbody>
</table>
Table VII. Excess heavy xenon isotopes in air and in natural gas

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Air</th>
<th>B-69</th>
<th>C-17</th>
<th>B-62</th>
<th>C-16</th>
<th>Novo Urei</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>0.000</td>
<td>1.4 ± 5.7</td>
<td>5.7 ± 5.9</td>
<td>8.5 ± 7.6</td>
<td>29.6 ± 17.4</td>
<td>-21.6</td>
</tr>
<tr>
<td>131</td>
<td>0.000</td>
<td>7.1 ± 4.0</td>
<td>10.8 ± 6.0</td>
<td>11.0 ± 5.8</td>
<td>45.5 ± 10.0</td>
<td>-18.1</td>
</tr>
<tr>
<td>132</td>
<td>0.000</td>
<td>6.8 ± 3.9</td>
<td>10.6 ± 3.9</td>
<td>14.1 ± 4.8</td>
<td>49.0 ± 13.4</td>
<td>-60.1</td>
</tr>
<tr>
<td>134</td>
<td>0.000</td>
<td>5.1 ± 2.0</td>
<td>21.5 ± 3.5</td>
<td>28.5 ± 2.7</td>
<td>73.1 ± 8.2</td>
<td>-77.0</td>
</tr>
<tr>
<td>136</td>
<td>0.000</td>
<td>17.9 ± 1.8</td>
<td>30.8 ± 3.7</td>
<td>34.5 ± 5.5</td>
<td>95.2 ± 7.8</td>
<td>-88.3</td>
</tr>
</tbody>
</table>

\[ \delta^1 = \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Sample}} - \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Air}} \times 1000 \]

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Air</th>
<th>B-69</th>
<th>C-17</th>
<th>B-62</th>
<th>C-16</th>
<th>Novo Urei</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>22.1</td>
<td>23.5 ± 5.8</td>
<td>25.9 ± 6.0</td>
<td>50.8 ± 7.7</td>
<td>52.4 ± 17.8</td>
<td>0.000</td>
</tr>
<tr>
<td>131</td>
<td>28.9</td>
<td>36.3 ± 4.2</td>
<td>40.0 ± 6.1</td>
<td>40.2 ± 5.9</td>
<td>75.7 ± 10.3</td>
<td>0.000</td>
</tr>
<tr>
<td>132</td>
<td>63.9</td>
<td>71.2 ± 4.2</td>
<td>75.2 ± 4.2</td>
<td>78.9 ± 5.2</td>
<td>111.6 ± 14.2</td>
<td>0.000</td>
</tr>
<tr>
<td>134</td>
<td>83.4</td>
<td>88.9 ± 2.1</td>
<td>106.7 ± 1.8</td>
<td>114.9 ± 1.0</td>
<td>162.6 ± 8.0</td>
<td>0.000</td>
</tr>
<tr>
<td>136</td>
<td>96.9</td>
<td>116.5 ± 2.0</td>
<td>116.7 ± 1.0</td>
<td>124.1 ± 6.0</td>
<td>201.3 ± 8.6</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[ \Delta^1 = \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Sample}} - \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Air}} \]

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Air</th>
<th>B-69</th>
<th>C-17</th>
<th>B-62</th>
<th>C-16</th>
<th>Novo Urei</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>0.000</td>
<td>0.009 ± 0.037</td>
<td>0.024 ± 0.038</td>
<td>0.038 ± 0.049</td>
<td>0.192 ± 0.113</td>
<td>-0.140</td>
</tr>
<tr>
<td>131</td>
<td>0.000</td>
<td>0.037 ± 0.021</td>
<td>0.056 ± 0.013</td>
<td>0.057 ± 0.030</td>
<td>0.236 ± 0.082</td>
<td>-0.146</td>
</tr>
<tr>
<td>132</td>
<td>0.000</td>
<td>0.045 ± 0.026</td>
<td>0.070 ± 0.026</td>
<td>0.093 ± 0.037</td>
<td>0.522 ± 0.085</td>
<td>-0.396</td>
</tr>
<tr>
<td>134</td>
<td>0.000</td>
<td>0.015 ± 0.015</td>
<td>0.045 ± 0.007</td>
<td>0.075 ± 0.006</td>
<td>0.166 ± 0.021</td>
<td>-0.177</td>
</tr>
<tr>
<td>136</td>
<td>0.000</td>
<td>0.039 ± 0.004</td>
<td>0.067 ± 0.008</td>
<td>0.077 ± 0.012</td>
<td>0.207 ± 0.017</td>
<td>-0.142</td>
</tr>
</tbody>
</table>

\[ \Delta^1 = \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Sample}} - \left( \frac{\text{Xe}^1}{\text{Xe}^{136}} \right)_{\text{Novo Urei}} \]
FIGURE I.
SAMPLE SIDE OF MASS SPECTROMETER

A-1 Preliminary titanium furnace
B Copper oxide furnace
C Air and sample spikes
T-1 Trap 1
V-1 Valve 1
D Ion gauge
T-2 Trap 2
E Tungsten filament
A-2 Main titanium furnace
F Charcoal finger
V-3 Valve 3
V-2 Valve 2

INSERT: Expanded view of typical air or sample spike

C-1 Glass encased metal slug

C-2 Break-off tip

C-3 Sample chamber
FIGURE II.

LOG FRACTIONATION FACTOR ($F^m$) FOR NOBLE GASES IN AIR, NATURAL GAS, AND IN THE MURRAY METEORITE VERSUS MASS NUMBER

$$F^m = \frac{(X^m/Xe^{130})_{\text{sample}}}{(X^m/Xe^{130})_{\text{cosmic}}}$$
FIGURE III.

PER MIL EXCESSES OF THE HEAVY XENON ISOTOPES
IN NATURAL GAS ABOVE AIR (PER MIL
DEFICIENCIES OF THE HEAVY XENON
ISOTOPES IN THE NOVO URSI METEORITE)
VERSUS MASS NUMBER
FIGURE IV.

PER MIL EXCESSES OF THE HEAVY XENON ISOTOPES IN AIR AND NATURAL GAS ABOVE NOVO UREI VERSUS MASS NUMBER
\[ \frac{\left( \frac{Xe^{130}}{Xe^{130}_{\text{Sample}}} \right)_{\text{Xe}^{130}}}{\left( \frac{Xe^{130}}{Xe^{130}_{\text{Xe}^{130}_{\text{Novo Urei}}} \right)_{\text{Xe}^{130}}} \times 1000 \text{ per mil} \]
FIGURE V.

EXCESSES OF THE HEAVY XENON ISOTOPES IN
NATURAL GAS ABOVE AIR (AND DEFICIENCIES OF THE
HEAVY XENON ISOTOPES IN THE NOVO UREI METEORITE)
VERSUS MASS NUMBER
FIGURE VI.

EXCESSES OF THE HEAVY XENON ISOTOPES IN AIR AND NATURAL GAS ABOVE THE NOVO URSI METEORITE VERSUS MASS NUMBER
FIGURE VII.

$\frac{Xe^{130}}{Xe^{132}}$ VERSUS $\frac{Xe^{136}}{Xe^{132}}$ IN AIR, NATURAL GAS, 
$^{235}U$ SPONTANEOUS FISSION, AND SELECTED METEORITES
"PRIMORDIAL" XENON

- Renazzo 600°C
- Bjurböle Matrix

TERRESTRIAL XENON

- Atmosphere
- Natural Gas - This Work
- Navajo - Clark and Thode
- Mitchell - Butler et al.

Extrapolates to
U$^{238}$ fissiogenic Xe

Extrapolates to
Pasamonte fissiogenic Xe
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VITA

Garry Anthony Bennett, son of Viola and Lester Bennett, was born December 6, 1942 in Sikeston, Missouri. He obtained his primary and secondary education in St. Louis County, Missouri.

He attended University of Missouri at Rolla, Missouri where he obtained his B.S. in chemistry in 1965. He entered graduate school at the University of Missouri at Rolla in September, 1965.

On September 3, 1966, he was married to the former Miss Jane Hanisch of Cedar Falls, Iowa.

He has held teaching assistantships continuously from September, 1965, and received a research assistantship from National Science Foundation, grant NSF GA-1462, in September, 1968.
APPENDIX I.

"XENON-134 FROM THE DECAY OF CESIUM-134"

Reprinted from Physical Review,
Volume 175, 1494 (1968)
Xenon-134 from the Decay of Cesium-134

E. C. Alexander, Jr., G. A. Bennett, B. Srinivasan, and O. K. Manuel

Reprinted from The Physical Review, Vol. 175, No. 4, pp. 1494, 20 November 1968
Xenon-134 from the Decay of Cesium-134

E. C. Alexander, Jr., G. A. Bennett, B. Srinivasan, and O. K. Manuel

Department of Chemistry, University of Missouri, Rolla, Missouri 65401

(Received 29 July 1968)

The production of Xe$^{134}$ from the decay of Cs$^{134}$ was determined by measuring the amount of Xe$^{134}$ in a pile-irradiated cesium salt. A branching ratio $(\lambda_{e.c.} + \lambda_{p})/\lambda_{p} = 4.5 \times 10^{-7}$ was obtained by comparing the excess Xe$^{134}$ with the Cs$^{134}$ activity.

The study of the concentration and isotopic composition of xenon in old terrestrial and meteoric samples has given many interesting clues to the early history of the earth and the solar system in general. Therefore, it is of interest to study those nuclear reactions which could produce xenon isotopes. Although mass data indicate that about 1.04 MeV is available for the Cs$^{134} \rightarrow$ Xe$^{134}$ transition, the decay of Cs$^{134}$ by electron capture or positron emission has not been reported. Keister et al. have set an upper limit of 1% for the electron capture branching ratio of Cs$^{134}$. Mims and Halban have reported an upper limit of $8.6 \times 10^{-4}$ for the positron-emission branching ratio. If the electron capture branching ratio were about 1% for Cs$^{134}$ then a particle irradiation of terrestrial or meteoritic material could conceivably alter the fractional abundance of Xe$^{134}$ since Cs$^{133}$ has an appreciable thermal neutron-capture cross section (30.6 b$^2$). In view of the possible importance of an electron capture or positron-emission branch in the decay of Cs$^{134}$ a direct measurement of the branching ratio was undertaken.

Two samples of approximately 0.65 g CsCl (Matthey Specpure grade) were encapsulated in Vycor, evacuated to $\approx 1 \times 10^{-7}$ mm Hg, sealed and irradiated together in a local reactor. The integrated neutron flux was $\approx 1.2 \times 10^{17}$ neutrons per cm$^2$. After allowing the samples to decay for four months, one of the ampules was attached to a Reynolds' type high-sensitivity mass spectrometer. The sample was melted under vacuum, and the xenon analyzed according to the method given by Alexander and Manuel.

The xenon isotopes were normalized to Xe$^{132}$ and the excess of mass number 134 was calculated from the equation

$$(Xe^{134}/Xe^{129})_{\text{sample}} - (Xe^{134}/Xe^{129})_{\text{atoms}} = \Delta_{134}.$$

The amount of excess Xe$^{134}$ produced per g of cesium was $(7.2 \pm 0.3) \times 10^{-11}$ cc STP. The Cs$^{134}$ content in the duplicate sample was determined by means of radiochemical techniques with a NaI scintillation counter. The counter was calibrated with a similar activity of a new liquid Cs$^{134}$ standard purchased from Nuclear Science and Engineering Corporation. From the Cs$^{134}$ activity in the duplicate sample, the number of Cs$^{134}$ atoms that had decayed at the time of the Xe$^{134}$ analysis was found to be $4.24 \times 10^{14}$ atoms per g of cesium. When combined with the Xe$^{134}$ excess the above value yields

$$\lambda_{e.c.} + \lambda_{p}/\lambda_{p} = 4.5 \times 10^{-7}.$$

The above value is thought to be accurate to about $\pm 10\%$ based on the statistical errors on the Cs$^{134}$ activity and the Xe$^{134}$ excess.

In view of the size of the branching ratio of Cs$^{134}$, this possible source of Xe$^{134}$ in naturally occurring samples is probably negligible.

We wish to thank M. Little and the reactor crew for their assistance with the irradiation of the samples and with the $\gamma$ counting.