

## Isotopic Variations in Terrestrial Xenon

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**Abstract.** Isotopic composition and amounts of xenon extracted from eclogite, from old granite, and from CO<sub>2</sub>-well gases have been measured. The Xe content of Bavarian eclogite is close to that of the earth (assumed to be outgassed), and this Xe exhibits no isotope anomalies. Xenon from several old granite samples from the central Transvaal contains substantial amounts of fissionogenic Xe from spontaneous fission of U<sup>238</sup>. Isotopic composition of this Xe is in agreement with values reported by Wetherill. The amount of fission Xe in samples from three related granites was very uniform, suggesting that U-Xe dating would be a valuable adjunct to K-Ar dating for old samples. Rough calculations of the U-Xe ages of these granites are in agreement with Rb-Sr ages obtained by Allsopp. Xenon from the CO<sub>2</sub>-well gases contained a component from spontaneous fission. The He<sup>4</sup>/Xe<sup>222</sup> ratio for this gas is very close to that expected for gas evolved from rocks with a Th/U ratio of 3. In addition, there was a small component of excess Xe<sup>136</sup>, i.e., Xe<sup>136\*</sup>/Xe<sup>136</sup> = 0.92 ± 0.42. Arguments are given to show that this residual Xe<sup>136</sup> is not due to fast or slow neutron absorption in Te<sup>136</sup>. The excess Xe<sup>136</sup>, if real appears to be due to decay, soon after formation of the earth, of now extinct 17-m.y. I<sup>136</sup>. The effect has far-reaching implications: (1) it implies that the outgassing of the interior of the earth is not complete and that even the decay products of some short-lived activities have not been homogenized; (2) calculations based on an extremely simple model (but one for which results are fairly representative) give a rough indication of the time interval by which the earth postdates the meteorites. It is clear that further experiments with well gases should be made to see whether the effect is reproducible.

### INTRODUCTION

In view of many interesting developments in the study of isotopic anomalies in Xe from meteorites (for recent accounts see, e.g., *Clarke and Thode* [1961], *Krummenacher et al.* [1962], *Zähringer* [1962]), it has seemed important to examine more closely the isotopic composition of Xe from various terrestrial sources. Of unusual interest is the question whether differentiation of the earth took place before complete decay of 17-m.y. I<sup>136</sup>, now known from meteorite studies to have been extant during the early history of the solar system. Another interesting question is whether any of the processes which led to the so-called general anomalies in isotopic composition of meteoritic Xe have left terrestrial traces.

Some terrestrial variations in Xe are already known. Xenon from old uranium-bearing minerals is enriched relative to the atmosphere in fission Xe [*Khlopin et al.*, 1947; *Macnamara and Thode*, 1950; *Wetherill*, 1953; *Fleming and Thode*, 1953]. Efforts to use Xe produced by fission for dating were reported by several workers [*Gerling and Shokoliukov*, 1959; *Gerling et al.*, 1959]. If the U concentration in such minerals is not excessive, the fission Xe is predominantly from spontaneous fission of U<sup>238</sup>, and it has been useful in determining spontaneous fission yields for this nuclide. Anomalous Xe has also been detected in old tellurium minerals; a slight excess of Xe<sup>222</sup> is attributed to double β decay of Te<sup>130</sup> [*Inghram and Reynolds*, 1950; *Hayden and Inghram*, 1951]. If the tellurium mineral was in association with U, there was also a marked excess of Xe<sup>136</sup> and Xe<sup>134</sup> from the (n, γ) reaction in Te. Aside from these studies there has been little investigation of isotope variations in terrestrial Xe.

In the present work we have examined xenon

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from three terrestrial sources. (1) Xenon from a Bavarian eclogite was examined as a sample which could possibly contain deep-seated terrestrial gas. (2) Xenon from three total-rock samples of the Old Granite of the central Transvaal was studied. These samples have been dated by the Rb-Sr method by *Allsopp* [1961]. The total-rock method gave consistent ages for the 3200-m.y.-old samples. Ages deduced from separated minerals from the samples varied, giving ages both higher and lower than the total-rock age and possibly reflecting a diffusion of Rb and Sr which occurred about 2000 m.y. ago, according to *Allsopp*. These samples were included in order to check whether any isotopic differences could be detected in ancient terrestrial Xe. *Cameron* [1962] has proposed a theory for the general anomalies in meteoritic Xe which includes the addition of anomalous Xe to the atmosphere of the earth by the solar wind. If this addition has been gradual, ancient terrestrial Xe might differ in isotopic composition from that in the present-day atmosphere. (3) Xenon from two CO<sub>2</sub>-gas-wells in Harding County, New Mexico, was examined. One of these gas samples (Mitchell no. 4) was studied for He and Ar by *Zartman et al.* [1961], who found a very high Ar<sup>40</sup>/Ar<sup>39</sup> ratio (22,500) and the lowest ratio of (He/Ar)<sub>radiogenic</sub> of any of the rock gases in that study. These data and the very high purity (99.9 per cent) of the CO<sub>2</sub> suggested to these authors that the gas was derived from the decomposition of carbonate rocks by intrusive basalt under conditions in which gases and liquids were expelled into the nearby sediments before the CO<sub>2</sub> accumulated. Under such conditions the Xe in the sample might be expected to reflect the isotopic composition of deep-seated terrestrial gas.

#### EXPERIMENTAL METHODS

All gas samples were analyzed statically in a glass mass spectrometer of high sensitivity [*Reynolds*, 1956] which utilizes a 60° wedge-shaped magnet of 4.5-inch radius. Ions were detected with an electron multiplier. An apparatus for extracting and purifying the samples was connected directly to the mass spectrometer. It was used to prepare the eclogite sample (see details below) and to repurify other gas samples which had been prepared on a separate vacuum line. Air samples of approximately 0.04 ccSTP

were purified in this sample system, and the extracted Xe was analyzed for calibration. The sensitivity of the spectrometer for Xe as determined by air runs at the time of the work was  $2 \times 10^{-23}$  ccSTP/mv. For short-term work this sensitivity factor remains constant to within about 20 per cent. For long-term work, we prefer to say that Xe quantities evaluated by this peak-height method are accurate to within a factor of 3. The air Xe samples were also used in determining the isotopic discrimination of the instrument, which results principally from influence upon gain of the electron multiplier by the stray field from the main spectrometer magnet. The discrimination curve for the Xe mass region is essentially a straight line when plotted versus mass number. An additional uncertainty in Xe isotope ratios of 2.5 per mil per mass unit difference must be assigned because of small fluctuations with time in the slope of this discrimination curve.

*Eclogite sample preparation.* (Sample: Silberbach, Fichtelgebirge, Bavaria, Germany. Crushed in diamond mortar to minus 28 mesh. A weight of 3.78 grams of 28-150 mesh fraction taken for analysis.) Since preliminary runs had shown the amount of Xe in the eclogite to be small, this sample was prepared directly in the sample system of the mass spectrometer, utilizing a gas-extraction 'bottle' developed for meteorite studies. The sample, wrapped in aluminum foil, was dropped into a thoroughly outgassed molybdenum crucible by magnetic release. An outgassed lid was then released so as to cap the crucible. The sample was melted by RF induction heating in two steps: an hour of 'degassing' at 800°C, as measured by a thermocouple imbedded in the base of the crucible, and a 30-minute 'melting run' at 1600°C. Gas from both heatings was examined, but the data presented are from the 'melting run' during which most of the gas was released. The gas was purified by exposure to hot titanium foil which was cooled in contact with the gas. The Xe fraction was isolated quantitatively by adsorbing it on activated charcoal at -70°C while the other rare gases were pumped away.

*Granite sample preparation.* (Samples: Crushed whole-rock samples of Old Granite, central Transvaal, South Africa, as follows: Witkoppen, 3.10 grams; Corlett Drive, 4.10 grams; Halfway House, 3.07 grams.) These samples

were melted in an outgassed auxiliary system which included a gas extraction bottle similar to that used in the eclogite run described above. The gas was purified by exposure in turn to hot CuO, a dry-ice trap, and hot (then cooled) Ti. The Xe fraction was isolated on charcoal at  $-78^{\circ}\text{C}$  in a Pyrex break-seal tube. Samples were repurified with Ti in the mass spectrometer sample system just before analysis.

*CO<sub>2</sub>-well sample preparation.* (Samples: Mitchell no. 4, about 50 ccSTP of gas from this well [Carbonic Chemicals Corp.] in the Beuyeros field, Harding County, New Mexico. Method of collection and chemical analysis (99.9 per cent CO<sub>2</sub>) are described by Zartman *et al.* [1961] under the designation of sample 16. Mitchell no. 7, about 160 ccSTP of gas from a well in the same field.) Xenon was extracted from these samples in a separate ultra-high vacuum line from which all chemicals were thoroughly outgassed before the sample was introduced. The CO<sub>2</sub> was reacted with hot KOH in a nickel reaction tube. The gas was also oxidized by passing it repeatedly over hot CuO, using chilled charcoal fingers to circulate the sample. The gas that remained was transferred to a section of the line where it was treated with hot (then cooled) Ti foil, destroying all but the rare gases. Xenon was finally isolated by adsorption on charcoal at  $-78^{\circ}\text{C}$  in a Pyrex break-seal tube. The Xe samples were repurified with Ti in the sample system of the mass spectrometer just before analysis.

#### RESULTS AND DISCUSSION

*Atmospheric xenon.* All xenon isotope ratios in this paper have been referred to the atmospheric isotope abundances tabulated by Strominger *et al.* [1958], based on Nier [1950].

*Eclogite sample.* Xenon from the 'melting run' on this sample was  $4 \times 10^{-11}$  ccSTP/g. If the earth is completely outgassed, its Xe content is  $6 \times 10^{-11}$  ccSTP/g. Assuming that Bavarian eclogite has a gas content characteristic of the mantle of the earth, we could infer from these data that the Xe content of the

earth, on the basis only of atmospheric Xe content, is correct to within a factor of 2.

The isotopic composition of this gas, given in Table 1, is normal within experimental error except at mass 124. Little weight can be given to the mass 124 datum in this single run because of the very small total sample. The total amount of Xe<sup>236</sup> analyzed was only about  $2 \times 10^{-18}$  ccSTP, or 6 million atoms. As the instrument is presently operated the apparent excess—25 per cent of this—is very close to the detectability for Xe.

Although atmospheric Xe occluded by the sample should have been largely removed by the preliminary heating, it is certain that a fraction of this gas was atmospheric Xe from outgassing of the apparatus. Thus the Xe content quoted above is an upper limit. It is still possible that eclogite contains very minute traces of Xe of abnormal composition. There are some eclogites for which formation at depth is entirely accepted by geologists. Bavarian eclogite is not, unfortunately, of this class. It would be desirable to extend this work to some of the eclogites with less disputed modes of origin.

*Granite samples.* Xenon from the Old Granites, central Transvaal, was analyzed at a time when hydrocarbon background interfered with analyses at masses 124 and 126. A large Xe<sup>236</sup> 'memory' from previous runs with very anomalous samples interfered to some extent with the analysis at mass 128. In other respects the analyses were satisfactory. Values of  $\delta_M^{(128)}$ , i.e., fractional variations in the *M* to 130 ratio in per mil referred to atmospheric Xe are listed in Table 2. The Xe<sup>236</sup> concentrations are also listed. The isotope 130 is used as a standard for  $\delta$  values because it is a 'shielded' isotope with respect to production by fission. All samples exhibit excess Xe at masses 131, 132, 134, and 136, which are the isotopes produced in fission. Ratios of the  $\delta$  values are listed in Table 3. If the samples consist of mixtures, in varying proportions, of anomalous Xe of some constant composition and of atmospheric Xe, the ratios of corresponding  $\delta$  values will be the same for all samples. This is

TABLE 1. Isotopic Composition of Xenon from Bavarian Eclogite  
 $\delta_M^{(128)} = 1000[(\text{Xe}^M/\text{Xe}^{128})/(\text{Xe}^M/\text{Xe}^{128})_{\text{atmos}} - 1]$  per mil

<i>M</i>	124	126	128	129	130	131	134	136
$\delta_M^{(128)}$	246 ± 60	-45 ± 60	12 ± 19	-15 ± 14	7 ± 19	-9 ± 10	-10 ± 12	21 ± 19

TABLE 2. Isotopic Composition and Amount of Xenon from Old Granites, Central Transvaal  
 $\delta_M^{(130)} = 1000[(X_e^M/X_e^{130})/(X_e^M/X_e^{130})_{atmos} - 1]$  per mil

Sample	Weight, grams	Mass, M						$[Xe^{136}]_{10^{-9}}$ ccSTP/g
		128	129	131	132	134	136	
Witkoppen Corlett	3.10	<57	4.3 ± 10	13.0 ± 10	34.0 ± 9	103.3 ± 10	142.8 ± 10	1.48
Drive	4.10	<30	-5.1 ± 8	5.9 ± 8	14.0 ± 7	43.3 ± 8	62.3 ± 8	3.64
Halfway House	3.07	<85	1.3 ± 7	14.3 ± 7	46.8 ± 5	172.9 ± 7	245.5 ± 9	0.91

seen to be true, within experimental error. Since the  $\delta$  values for Halfway House are substantially more precise than the others, they have been used in our calculations.

In Table 4 the  $\delta$  values have been converted to excess-Xe ratios by assuming that the gas consists of an atmospheric component (contributing all the  $Xe^{130}$ ) plus an excess component. This permits a comparison with Xe produced in spontaneous fission of  $U^{238}$  [Wetherill, 1953], also tabulated. Within experimental error these isotope ratios in Table 4 are seen to be identical, so that all the excess Xe in these samples can be attributed to this source.

The amounts of excess  $Xe^{136}$ , expressed in millivolts of mass-spectrometer output per gram of sample, appear in Table 5. These amounts are remarkably constant for all three samples. The three mass-spectrometer analyses were made successively within a 48-hour period, so that the sensitivity of the instrument could be expected to remain quite constant throughout the series of runs. We conclude that the fission Xe component in these three granites is constant to within our present ability to measure this quantity. Applying our sensitivity factor of  $2 \times 10^{-15}$  ccSTP/mv

 TABLE 3. Ratios of  $\delta$  Values for Old Granites, Central Transvaal

Sample*	$\frac{\delta_{131}^{(130)}}{\delta_{136}^{(130)}}$	$\frac{\delta_{132}^{(130)}}{\delta_{136}^{(130)}}$	$\frac{\delta_{134}^{(130)}}{\delta_{136}^{(130)}}$
Witkoppen Corlett	.0910 ± .07	.238 ± .07	.723 ± .086
Drive	.095 ± .13	.225 ± .11	.695 ± .156
Halfway House	.058 ± .028	.191 ± .02	.705 ± .038

\* There are no significant differences among the xenon samples in this respect.

we obtain an average fissionogenic  $Xe^{136}$  content,  $Xe^{136}_F$ , of  $7.0 \times 10^{-12}$  ccSTP  $Xe^{136}_F$  per gram.

These results indicate that with refined techniques U-Xe dating of old granites is feasible. The age is computed from

$$t = \tau \ln [(Xe^{136}_F/U^{238}) \cdot 1/\alpha_F \cdot 1/y_{136} + 1]$$

where  $\tau$  is the mean life of  $U^{238}$  ( $6.49 \times 10^9$  years),  $\alpha_F$  is the fraction of decays by spontaneous fission ( $0.57 \times 10^{-6}$ ), and  $y_{136}$  is the fission yield of  $Xe^{136}$  in this process. Assuming  $y_{136} = 0.06$  and a U content of 3.7 ppm (based on the recommended value for standard granite G-1; see, e.g., the compilation of Fleischer and Stevens [1962]) we find

$$t = 3.0_{-1.3}^{+3.7} \times 10^9 \text{ years}$$

The error on this age is very large because of the probably over-generous error of a factor of 3 we have assigned to the spectrometer sensitivity, but the result is in very satisfactory agreement with the age of  $3.2 \times 10^9$  years measured by the Rb-Sr method [Allsopp, 1961].

The possibility of a new rare-gas method for dating old rocks is not without importance. At present much dating of old rocks is done by the K-Ar method, but because of frequent instances of Ar leakage in old rocks such determinations require checking by another method of dating (e.g. Rb-Sr or U-Pb). The U-Xe method would probably serve as an adequate check, since Xe leakage can be expected to differ substantially from Ar leakage; concordance would then indicate a closed system. Extraction and purification procedures for radiogenic Ar retain a fissionogenic Xe as well, so that in one sense the U-Xe method can be said to be partially 'built-in' to the K-Ar method.

*CO<sub>2</sub>-well samples.* The isotopic composition

TABLE 4. Comparison of Excess Xenon Components in Halfway House, Old Granite with Xenon from Spontaneous Fission of U<sup>238</sup>

Sample*	(Xe <sup>129</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>131</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>132</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>134</sup> /Xe <sup>136</sup> ) <sub>excess</sub>
Halfway House	.016 ± .085	.138 ± .067	.579 ± .061	.830 ± .045
U <sup>238</sup> spont. fission [Wetherill, 1953]	<.002	.076 ± .003	.595 ± .010	.832 ± .012
Difference	.016 ± .085	.062 ± .067	-.016 ± .062	-.002 ± .047

\* The xenon samples are indistinguishable in this respect.

of Xe from the CO<sub>2</sub> wells is given in Table 6. In Mitchell no. 7 well there are seen to be significant isotopic anomalies at masses 126, 130, 131, 134, and 136, if mass 132 is used as the reference isotope. All these anomalies occur also in Mitchell no. 4 well, although they are smaller there and, as in the case of mass 131, not always significant. The test of whether the two samples of

two analyses are thus consistent with the existence of a single kind of anomalous Xe in these rock gases—differences in  $\delta$  values arise because of differing degrees of dilution with atmospheric Xe.

Again a 'fission pattern' is suggested by the data, so that the choice of Xe<sup>130</sup> as the standard isotope is to be preferred. Unfortunately, the analysis of gas from Mitchell no. 4 is useless here because we were able to obtain only an upper limit to the amount of Xe<sup>130</sup> in the sample (i.e.,  $\delta_{130}^{(132)} < -6.6$ ). Bad resolution of the mass spectrometer in the run on Mitchell no. 4 caused interference at mass 130 with the adjacent masses. (This difficulty, which has occurred intermittently in runs with the glass mass spectrometer, has been traced to faulty conducting coating on a portion of the glass analyzer tube and has since been corrected.) Mass 128 is totally inadequate as a standard isotope in the present work because of the large memory effect referred to above. In the following discussion, then, we are restricted to the data for Mitchell no. 7.

In Table 7 we present the isotopic composition of Xe from Mitchell no. 7, referred to Xe<sup>130</sup> as the reference isotope. When so presented there appear to be excess amounts of Xe at masses 129, 131, 132, 134, and 136. In Table 8 these data

TABLE 5. Excess Xe<sup>136</sup> Content of Old Granites, Central Transvaal

Sample	Excess Xe <sup>136</sup> content (spectrometer millivolts/gram)*
Witkoppen	3.37 ± 0.40
Corlett Drive	3.69 ± 0.66
Halfway House	3.53 ± 0.30
Average	3.51 ± 0.24

\* Spectrometer sensitivity is approximately  $2 \times 10^{-23}$  ccSTP/millivolt.

Xe differ only in their content of atmospheric Xe is to determine whether the ratio of a  $\delta$  value for one sample to the corresponding  $\delta$  value for the other sample is the same for all isotopes. This ratio has been computed whenever significant and is consistent with  $\delta(\text{no. 4})/\delta(\text{no. 7}) = 0.5$ , within experimental error, for all isotopes. The

TABLE 6. Isotopic Composition of Xenon from CO<sub>2</sub> Wells, Harding County, New Mexico  
 $\delta_M^{(132)} = 1000[(\text{Xe}^M/\text{Xe}^{132})/(\text{Xe}^M/\text{Xe}^{132})_{\text{atmos}} - 1]$  per mil

	Mass, M							
	124	126	128	129	130	131	134	136
Mitchell no. 4	-30.8 ± 35	-65.7 ± 24	4.2 ± 50	-3.1 ± 9	< -6.6	-3.8 ± 5	15.5 ± 5	30.3 ± 10
Mitchell no. 7	-5.6 ± 28	-35.5 ± 21	-14.3 ± 23	3.8 ± 8	-19.7 ± 6	-7.7 ± 5	32.7 ± 8	56.1 ± 10
Ratio no. 4/no. 7 (where significant)		1.8 ± 1.3					.47 ± .18	.54 ± .20

TABLE 7. Isotopic Composition of Xenon from Mitchell No. 7 CO<sub>2</sub> Well, Referred to Xe<sup>136</sup> as Reference Isotope

$$\delta_M^{(130)} = 1000[(Xe^M/Xe^{130})/(Xe^M/Xe^{130})_{atmos} - 1] \text{ per mil}$$

M	124	126	128	129	131	132	134	136
$\delta_M^{(130)}$	14.4 ± 29	-16.1 ± 22	5.5 ± 24	24.0 ± 10	12.2 ± 8	20.1 ± 6	53.5 ± 10	77.3 ± 12

have been transformed to excess-Xe ratios for comparison with fission Xe from U<sup>238</sup> spontaneous fission and from U<sup>235</sup> slow-neutron fission. The excess Xe from the sample closely resembles fission Xe from spontaneous fission of U<sup>238</sup>. An appreciable contribution from slow-neutron fission of U<sup>235</sup> is ruled out by the high Xe<sup>124</sup>/Xe<sup>136</sup> ratio in the latter: it is highly unlikely that more than 5 per cent of the Xe<sup>136</sup>, is from that source. Accordingly, the component ascribed to spontaneous fission has been subtracted in Table 8. There remains a residue at mass 129 (129 residue/136 excess = 0.92 ± 0.42) and possibly at mass 131 (131 residue/136 excess = 0.30 ± 0.26).

We shall discuss the fission component first. The gas from the Mitchell wells is known [Zartman *et al.*, 1961] to contain 45 ppm radiogenic He<sup>4</sup>. This is about 57 per cent from  $\alpha$  decay of U<sup>238</sup> and its daughters if, as is most likely, the source is ascribed to relatively recent production in the rocks with Th/U = 3. This amount of He<sup>4</sup> should be accompanied by (0.57) (45 × 10<sup>-6</sup>) (0.57 × 10<sup>-6</sup>) (0.06)/8 = 1.1 × 10<sup>-12</sup> atom fraction Xe<sup>136</sup>. The total Xe content of gas from Mitchell no. 7 is, subject to the rather large possible error in mass-spectrometer sensitivity discussed earlier, 13 × 10<sup>-12</sup> atom fraction. This corresponds to an excess Xe<sup>136</sup> content of 0.9 × 10<sup>-12</sup> atom fraction. Within experimental error,

this constitutes total agreement with the Xe<sup>136</sup> predicted from spontaneous fission.

Turning finally to the residual Xe<sup>136</sup> component, we recognize three possibilities. First, the residual is not real. This is possible but not likely because the effect (Xe<sup>129</sup><sub>residue</sub>/Xe<sup>136</sup><sub>excess</sub> = 0.92) is more than twice the assigned error, 0.42. Unfortunately, the run on Mitchell no. 4 is inconclusive on this point. If the weighted average of the ratios of  $\delta$ 's from Table 6 is used to reconstruct the missing  $\delta_{129}^{(136)}$  for Mitchell no. 4, we can compute the 129 residue for that run. The result (Xe<sup>129</sup><sub>residue</sub>/Xe<sup>136</sup><sub>excess</sub> = 0.52 ± 0.85) supports the effect, but not significantly.

The second possible explanation of the residual Xe<sup>136</sup> is that it is real and is to be attributed to the (n,  $\gamma$ ) reaction on Te<sup>136</sup>. The neutrons at great underground depths originate from spontaneous fission of U<sup>238</sup> and from ( $\alpha$ , n) reactions induced by U and Th  $\alpha$  particles [Wetherill, 1953; 1954]. Eugster [1954] has shown that such neutrons are more abundant than cosmic-ray neutrons at great depths underground: the flux of neutrons detected in boron-loaded nuclear emulsions was 26 times greater in a tunnel under 2100 meters of rock than at the surface of the earth at Berne, Switzerland. Inghram and Reynolds [1950] showed that neutrons from U can indeed produce excess Xe<sup>136</sup> in Te; they found an excess of both Xe<sup>136</sup> and Xe<sup>134</sup> in an ancient

TABLE 8. Comparison of Excess Component in Xenon from Mitchell No. 7 CO<sub>2</sub> Well with Xenon from Spontaneous Fission of U<sup>238</sup> (and from Neutron Fission of U<sup>235</sup>)

Sample	(Xe <sup>129</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>131</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>128</sup> /Xe <sup>136</sup> ) <sub>excess</sub>	(Xe <sup>134</sup> /Xe <sup>136</sup> ) <sub>excess</sub>
Xe from CO <sub>2</sub> well	.92 ± .42	.377 ± .26	.788 ± .30	.814 ± .19
U <sup>238</sup> spont. fission	<.002	.076 ± .003	.595 ± .010	.832 ± .012
(U <sup>235</sup> neutron fission)	(.139)	(.454)	(.678)	(1.248)
Difference*	.92 ± .42	.301 ± .26		

\* There is an apparently significant residue of Xe<sup>129</sup> after subtraction of U<sup>238</sup> spontaneous fission xenon.

tellurium mineral which had been in association with U. *Hayden and Inghram* [1951] showed that a tellurium mineral of similar age, which had not been in association with U, did not contain comparable amounts of excess  $Xe^{136}$  and  $Xe^{138}$ . In the *Inghram-Reynolds* experiment the ratio of  $Xe^{136}$  to  $Xe^{138}$  was 3.0. From thermal neutron cross sections we should expect this ratio to be 0.6 if thermal neutrons were responsible. This disparity suggests that fast neutrons are responsible for the production of the Xe isotopes. Let us suppose for the moment that fast neutrons are responsible. There are  $2.4 \pm 0.2$  fast neutrons emitted from spontaneous fission of  $U^{238}$  [Littler, 1952]. We can estimate the number of additional neutrons from  $(\alpha, n)$  reactions from *Roberts'* [1947] data, tabulated by *Anderson* [1948], on the neutron yields from thick targets bombarded by polonium  $\alpha$  particles. Assuming that the U resides in a rock of granitic composition, we expect 0.18 neutron per  $10^6 \alpha$  particles, using *Roberts'* values for neutron yields in O, Si, Al, Mg, and Na. This gives 2.6 additional neutrons per spontaneous fission; *Wetherill* [1953] came to similar conclusions for Madagascar euxenite. Another 1.9 neutrons per spontaneous fission would arise from Th  $\alpha$  particles in a rock where the Th/U ratio is 3. Combining, we expect  $2.4 + 2.6 + 1.9 = 6.9$  neutrons per spontaneous fission. Since the spontaneous fission yield for  $Xe^{136}$  is about 6 per cent, there will be  $6.9/0.06 = 115$  neutrons per  $Xe^{136}$ -producing fission. Since we have seen that the 129 residue/136 excess = 0.92, we conclude that, if the  $Xe^{136}$  residue is due to neutron absorption by  $Te^{136}$ , this reaction must occur once for every  $115/0.92 = 125$  neutrons. We can estimate the least possible Te content which would lead to this result in the following way. *Gibbons et al.* [1961] have plotted average neutron capture cross sections near 65 keV as a function of  $Z$ . For Si the average cross section is about 2.1 millibarns. If we suppose that the rock is 50 per cent  $SiO_2$  and  $x$  ppm Te,  $(N\sigma)_{Te^{136}}$  must be at least  $1/125 \times (N\sigma)_{Si^{28}}$ . For  $Te^{136}$ ,  $\sigma \approx 125$  millibarns. From this we conclude  $x > 450$  ppm.

This far exceeds any conceivable concentration of Te in granite or diabase, where we might expect it to lie in the range 2 to 20 ppm. It appears that formation of the  $Xe^{136}$  residue from fast neutrons can be excluded.

Formation of this residue from absorption by

$Te^{136}$  of thermal neutrons can also be excluded by the following argument. It is very unlikely that slow-neutron fission of  $U^{235}$  has contributed more than 0.1 per cent of the excess  $Xe^{136}$ . This upper limit can be set by supposing that all the neutrons from U and Th are moderated and then captured either by Na or by  $U^{235}$ . By neglecting the absorption of fast neutrons and the competing absorption of slow neutrons in elements other than Na, we are greatly exaggerating the fraction absorbed in  $U^{235}$ . Since there are 6.9 neutrons (see above) per spontaneous fission, there are  $6.9/0.06 = 115$  neutrons per  $Xe^{136}$ , produced by spontaneous fission. Assuming 2 per cent Na ( $\sigma = 0.53$  barns) and 3 ppm U ( $\sigma = 582$  barns for fission of  $U^{235}$ ) we find  $(Xe^{136})_{neutron}/(Xe^{136})_{spont.} \leq 0.8 \times 10^{-6}$ . We get an experimental measure of the maximum contribution of slow-neutron fission of  $U^{235}$  from the data on  $(Xe^{134}/Xe^{136})_{excess}$  in Table 8. The percentage of  $Xe^{136}$  due to slow-neutron fission deduced from the data in Table 8 is 0<sup>+0.2</sup>-0 per cent. The theoretical upper limit is much below the experimental one, and so we use the former in the calculation that follows. Returning to the question of  $Xe^{136}$  from slow neutrons on  $Te^{136}$ , and taking 10 as a reasonable terrestrial value for the Te/U atomic ratio (based on values by *Goles and Anders* [1962] for this ratio in various classes of meteorites), we would expect the ratio of production of  $Xe^{136}$  from  $Te^{136}$  ( $\sigma = 0.14$  barn) to  $Xe^{136}$  from  $U^{235}$  fission ( $\sigma = 582$  barns,  $Xe^{136}$  yield = 6 per cent) to be 1.8. But as we have seen, the ratio based on measurement of excess  $Xe^{136}$  and calculation concerning excess  $Xe^{136}$ , is greater than  $(0.92 - 0.42)/10^{-6} = 500$ . We have subtracted the probable error of 0.42 from the value 0.92 in order to arrive at a conservative number. The discrepancy between 1.8 and  $\geq 500$  requires some mechanism other than slow-neutron absorption on  $Te^{136}$  for the  $Xe^{136}$  production.

The third possible explanation of the excess  $Xe^{136}$  is that it was produced by the decay of 17-m.y.  $I^{136}$  very early in the history of the earth. This would mean that the outgassing of the earth's interior is incomplete and that the decay products of such short-lived elements as  $I^{136}$  have not been homogenized. This suggests that  $Xe^{136}$  and possibly other such daughter isotopes are presently being added to the atmosphere and the upper crust. It follows that thorough con-

vective mixing and outgassing did not occur during the early stages in the differentiation of the earth.

It is instructive to attempt to calculate a 'formation interval' for the earth, assuming the excess  $Xe^{129}$  to be from  $I^{129}$  decay. The formation interval for a system is defined as the time interval between the end of nucleosynthesis and the point in time when the system began quantitatively to retain radiogenic  $Xe^{129}$ . We suppose that the system has been closed with respect to U, I, and daughter Xe for  $4.6 \times 10^9$  years. We shall suppose that the atomic ratio I/U is 10 on the basis of meteoritic values by *Goles and Anders* [1962]. Then

$$\frac{Xe^{129*}}{I^{127}} = \left( \frac{U^{238}}{I^{127}} \right) \times \left( \frac{Xe^{136}_f}{U^{238}_f} \right) \times \left( \frac{Xe^{129*}}{Xe^{136}_f} \right)$$

The first expression on the right-hand side is 0.1 by hypothesis, the second is  $3.4 \times 10^{-8}$  from decay constants of U and the assumed age of  $4.6 \times 10^9$  years, and the third is 0.92 by measurement. Thus  $Xe^{129*}/I^{127} = 3.1 \times 10^{-9}$ .

If we take as the ratio of  $I^{129}/I^{127}$  at the end of nucleosynthesis the value 0.00125 given by continuous galactic synthesis over an effective period of  $20 \times 10^9$  years [Cameron, 1962], we obtain a formation interval of 320 m.y.

This formation interval cannot be taken very seriously in an absolute sense if we stop to consider the role which  $Pu^{244}$  would play in this scheme. Present at the end of nucleosynthesis with an abundance of about 1/60 of  $U^{238}$  it would generate about twenty times as much spontaneous fission Xe in our system as is generated by  $U^{238}$ . Since it seems very likely from the isotopic composition of the fission component and from the  $Xe_f^{136}/He^4$  ratio that it was produced by spontaneous fission of  $U^{238}$ , we probably cannot adopt both our simple closed model and the hypothesis of galactic synthesis. If the  $I^{129}$  were produced by some process which did not produce  $Pu^{244}$  along with it [Fowler *et al.*, 1962] and if its production in meteorites was the same relative to  $I^{127}$  as in the terrestrial material, the difference in formation intervals calculated for meteorites and the earth would be significant. Latest results for the formation intervals of stone meteorites [Reynolds, 1963] give values in the range 35 to 52 m.y. This suggests that the earth postdates the meteorites by about 270 m.y. Even this conclusion cannot be given much

weight at present because of the extreme nature of the assumptions made in setting up the closed-system model, but the general character of the computation is instructive.

*Note added in proof.* We have just seen a thesis by W. B. Clarke (McMaster University, 1963), who has examined, among other things, gas from a helium well in which there was a substantial fission Xe component. He finds values of  $(Xe^{136}/Xe^{130})_{\text{excess}}$  and  $(Xe^{136}/Xe^{129})_{\text{excess}}$ , which, like those in Table 8, are higher than for spontaneous fission of  $U^{238}$  as determined by Wetherill, but which in his work cannot be dismissed as a result of experimental error. He has noted similar and very striking examples of excess  $Xe^{136}$  and  $Xe^{130}$  in the first few per cent of gas released by heating from neutron-irradiated U compounds; there the excess can be explained if the radioactive precursors of the fission Xe diffuse preferentially in the lattice of the U compound. To invoke this mechanism to explain the composition of fission Xe in gas wells requires rather special circumstances for the outgassing of Xe from rocks. Clarke also notes a hint of excess  $Xe^{129}$  in his sample, which is in agreement with our work on an absolute basis for gas content, but not on a relative basis—i.e., when referred to the fission component which is much more abundant in the well he studied. We are grateful to Dr. Clarke for the opportunity to see his data before the publication of his paper.

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