This is shown in Fig. 2, from which we conclude that fertilizer nitrogen contributed 55 ± 10 percent of the nitrate entering Lake Decatur during the spring months of 1970.

We have assumed that the nitrogen transformations in the soil do not significantly discriminate between ^{14}N and ^{15}N, so that the ^{15}N : ^{14}N ratio observed in the effluent nitrate reflects the ^{15}N: ^{14}N ratio of the source nitrogen. In fact, almost all the biological nitrogen transformations in the soil do have an isotope effect. A quantitative correction for these isotopic fractionations is not yet possible. It is possible, however, to predict the direction of the isotope fractionation in each nitrogen transformation from data already available (*3*). With one exception, these effects are such that they tend to minimize the apparent contribution of fertilizer nitrogen to surface water nitrate. The exception, nitrogen fixation, contributes only a small quantity of nitrogen compared with the fertilizer nitrogen. On these grounds, we regard our estimate of 55 ± 10 percent to be a minimum.

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7. Although $\delta^{15}N = +3.7$ for anhydrous ammonia, we used the value of +3 since other forms of nitrogen fertilizer used in the region had values of $\delta^{15}N$ closer to zero. The value +3 is taken to reflect the estimated average, weighted for relative use.
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10. This requires one additional assumption, that the nitrate mineralized from the soils of the region is accurately characterized by the measurements made at one point in the 900-square-mile watershed. Two arguments support this assumption: (i) the soils of the watershed are relatively uniform and (ii) if $\delta^{15}N = +13$ were not representative of the entire upper-Sangamon watershed, then the only way in which the surface water data could fall on the regression line established by the tile water drained from a small subregion (about 1 square mile) of the drainage basin would be by chance.
11. This work was supported in part by PHS grant ES-00139.

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The Xenon Record of Extinct Radioactivities in the Earth

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

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

The half-lives of ^{129}I and ^{244}Pu are 17 × 10^6 (*4*) and 82 × 10^6 (*5*) years, respectively, and their decay products identified in meteorites are radiogenic ^{129}Xe (^{129r}Xe) from ^{129}I and fissiogenic $^{131\text{-}136}$Xe ($^{131\text{-}136f}$Xe) from ^{244}Pu. Because it is not possible to calculate the age of a body solely from the concentration of a stable decay product, total meteorite ages cannot be obtained by either ^{129}I-^{129r}Xe or ^{244}Pu-$^{131\text{-}136f}$Xe dating. However, early ^{129}I : ^{127}I and ^{244}Pu : ^{238}U ratios in meteorites decreased rapidly because of the shorter half-lives of the nuclides in the numerator, and since the nuclides in each ratio display similar geochemical behavior, measurements of the ^{129r}Xe : ^{127}I and $^{131\text{-}136f}$Xe : ^{238}U ratios present in meteorites today are used to define the ^{129}I : ^{127}I and ^{244}Pu : ^{238}U ratios present when the meteorites formed (*6, 7*). For example, it has been found that chondrite meteorites were formed when the ^{129}I : ^{127}I ratio was about 1.1 × 10^{-4} (*8*) and the ^{244}Pu : ^{238}U ratio was about 0.013 (*7*). In several different achondrites the initial ^{129}I : ^{127}I ratio was found to vary from 10^{-8} to 10^{-5}, and the initial ^{244}Pu : ^{238}U ratio varied from 0.002 to 0.006 (*9*), which suggests that the achondrites formed later than the chondrites. Meteorite age differences of a few million years have been detected by measurements of ^{129r}Xe : ^{127}I and $^{131\text{-}136f}$Xe : ^{238}U ratios (*9, 10*).

The chronology of early events for the earth is not so well established. The earth's interior is inaccessible, and the rocks and minerals of the earth's crust show a wide range of ages with an upper limit of about 3.5 × 10^9 years. Further, the continuous formation of new crustal material along oceanic ridges suggests that even today the earth's crust is not completely isolated from its mantle. Thus, the fundamental assumption of all radioactive dating, that the system has remained isolated or closed over the time period being measured, may not be valid for the accessible portions of the earth. Age estimates of the earth based on ^{207}Pb : ^{206}Pb ratios are undoubtedly among the more reliable since chemical fractionation would alter neither the ratio of the two parents, ^{235}U : ^{238}U, nor the ratio of the decay products, ^{207}Pb : ^{206}Pb. The

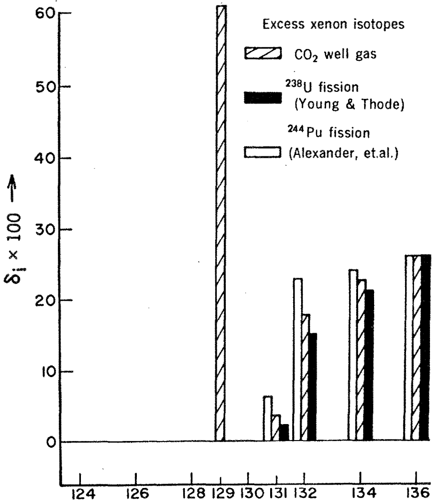

Fig. 1. The excess xenon isotopes found in CO_2 gas wells relative to atmospheric xenon (*16*). The excess for each isotope of mass number i is expressed as δ_i, which is defined by Eq. 1 (see text). The enrichment at each mass number is compared with that expected from the fission of ^{244}Pu (*20*)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

Table 1. Xenon in samples of CO_2 well gas and in air. Volumes are given at standard temperature and pressure.

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

^{207}Pb : ^{206}Pb ratios in oceanic sediments, lead ores, and old shield-area rocks suggest that the earth is approximately the same age as meteorites (*2*, *11*). Even so, no clear evidence has previously been presented for the occurrence on earth of the decay products of the extinct radioactivities, ^{129}I or ^{244}Pu.

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

Within the limits of statistical error, the isotope ratios from these two analyses are identical and correspond to atmospheric xenon at all mass numbers except 129, 132, 134, and 136. The abundance pattern of the xenon isotopes relative to that in the atmosphere (*16*) does not fit the pattern expected from isotopic fractionation (*17*). The ^{129}Xe isotope is enriched by about 10 percent over its atmospheric abundance, and the ^{136}Xe isotope is enriched by about 12 percent. The amount of excess ^{129}Xe we attribute to the decay of now extinct ^{129}I and show this as ^{129r}Xe near the bottom of Table 1. In a similar manner the amount of excess ^{136}Xe we attribute to fission decay and designate this as ^{136f}Xe. We are certain that both of these anomalies are real and that terrestrial xenon therefore contains a record of extinct elements that were present in the very early history of the earth.

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

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

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

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

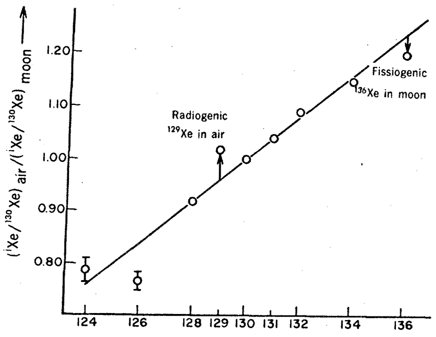

Fig. 2. The ratio of xenon in air (*16*) to xenon released from lunar soil at 800°C (*25*). The line shows the effects of isotopic fractionation. Deviations from isotopic fractionation at ^{129}Xe and ^{136}Xe are due to radiogenic ^{129}Xe in air and fissiogenic ^{136}Xe in the moon, respectively.

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

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

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

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

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

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Carbonic Anhydrase Interaction with DDT, DDE, and Dieldrin

Abstract. *The active site of various carbonic anhydrases is not blocked by DDT, DDE, or dieldrin. Impairment of catalytic efficiency can only be documented in opalescent test solutions in which the insecticides are present in excess of their solubility limit. These slowly forming precipitates occlude enzyme from solution and furnish a physical explanation of the supposed inhibition. The amounts occluded depend, among other things, on the conformational and topographical characteristics of the particular carbonic anhydrase molecules.*

The transfer of carbon dioxide from one part of the organism to another is often limited by the rate of hydration of carbon dioxide to form bicarbonate ion, and by the reverse process of dehydration of the latter substance (*1*). Under physiological *p*H the hydration of CO_2 and the dehydration of HCO_3^- are relatively slow processes (*2*), a fact which has imposed the biological necessity for developing an enzyme to accelerate these reactions in many kinds of