

Origin of the Elements: Pre-Fermi Reactor and Plutonium-244 in Nature

PAUL K. KURODA

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received May 10, 1978

Theodore W. Richards¹ stated in 1919: "If our inconceivably ancient Universe even had any beginning, the conditions determining that beginning must even now be engraved in the atomic weights. They are the hieroglyphics which tell in a language of their own the story of the birth or evolution of all matter, and the Periodic Table containing the classification of the elements is the Rosetta Stone, which may enable us to interpret them."

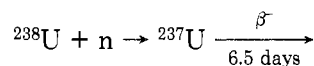
There are three places in the periodic table where the order of the atomic number and the atomic weight is reversed. It occurs, for example, in the sequence Te, I, and Xe: the atomic weight of I is smaller than that of Te. These anomalies could not be fully explained in the days of Richards, but in 1919 Francis W. Aston constructed the first mass spectrograph, which enabled one to determine the relative abundances of the stable isotopes of the elements. It thus became possible to measure quite accurately not only the "average" weights of the elements, but also the exact isotopic compositions. Modern versions of Aston's mass spectrograph are now being used by many researchers in their explorations into the origin of the elements in the Universe.

Aston visited Japan in the summer of 1936 to deliver a lecture at the Imperial University of Tokyo. As a 19-year old student, I attended the lecture and listened to what he had to say. It appears that Aston was fearful of the possibility that an enormous amount of energy released by the conversion of matter may somehow engulf the entire earth. He thus concluded his December 12, 1922, Nobel Lecture with the following remarks:² "Should the research workers of the future discover some means of releasing this energy in a form which could be employed, the human race will have at its command powers beyond the dreams of scientific fiction; but the remote possibility must always be considered that the energy once liberated will be completely uncontrollable and by its intense violence detonate all neighboring substances. In this event the whole of the hydrogen on the earth might be transformed at once and the success of the experiment published at large to the Universe as a new star."

In 1935, Frédéric Joliot³ also expressed a similar view when he stated: "A star invisible to the naked eye may become very brilliant and visible without any telescope—the appearance of a Nova. This sudden flaring up of the star is perhaps due to transmutations of an explosive character like those which our wandering

imagination is perceiving now—a process that the investigators will no doubt attempt to realize while taking, we hope, the necessary precautions."

During World War II, nuclear physicists and chemists in the United States and in Japan were both attempting to produce a nuclear transformation of an explosive character. The Japanese team led by the physicist Yoshio Nishina and the chemist Kenjiro Kimura was investigating the reaction



but they were unable to positively identify the decay product of ²³⁷U: an isotope of the then unknown element 93.

Contrary to the generally held view, however, it appears to me that the leaders of the Japanese team were not really interested in building a nuclear weapon. In a secret Imperial Army Document dated July 6, 1943, for example, Nishina expressed the following opinion: "An assemblage of 10 kilograms of ²³⁵U and 30 kilograms of water would produce an energy equivalent to that of 10,000 metric tons of coal. Although it may be rather difficult to use the uranium in ordinary engines, it can be easily used as a bomb. However, 10 kilograms of the ²³⁵U will be lost and hence we must always have an additional 10 kilograms of this substance ready. Therefore, the use of uranium as a nuclear weapon appears at this time to be *unwise*."

I was asked by my major professor, Kenjiro Kimura, of the Imperial University of Tokyo to undertake geochemical investigations on volcanoes and hot springs of Japan. I thus became interested in the problems related to large-scale processes occurring in the interior of the earth crust. I often wondered if the events taking place in the earth crust might not be *nuclear* rather than *chemical* processes. I also imagined that some unknown heavy elements which existed in the early history of the earth might have played a role as a source of energy for the volcanic activities.

I was particularly intrigued by a paper published by a young American chemist named Willard F. Libby⁴ in 1939. He put forward the idea that natural fission might be detected by disparities between the results of various calculations of the age of the oldest rocks based on the observed abundances of the elements and the intensities of the ordinary radioactive emissions from uranium and thorium. The extremely long half-life observed for the natural fission of uranium, however,

(1) Theodore W. Richards, "Atomic Weights", Nobel Lecture, Dec 6, 1919.

(2) Francis W. Aston, "Mass Spectra and Isotopes", Nobel Lecture, Dec 12, 1922.

(3) Frédéric Joliot, "Chemical Evidence of the Transmutation of Elements", Nobel Lecture, Dec 12, 1935.

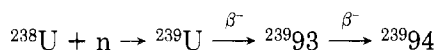
(4) W. F. Libby, *Phys. Rev.*, **55**, 1269 (1939).

Paul K. Kuroda is Professor of Chemistry at the University of Arkansas. He was born in Fukuoka, Japan, and educated at Tokyo (Imperial) University. After receiving his D.Sc. there in 1944, he was appointed to the faculty. He left Tokyo in 1949 for the United States, and was at first a research associate at the University of Minnesota before moving to the University of Arkansas. This Account is based on Professor Kuroda's Award address for the 1978 ACS Nuclear Applications in Chemistry Award sponsored by G. D. Searle & Co.

seemed to exclude such a possibility. Thus in 1939, Libby concluded: "The agreement between the uranium and thorium age determinations on old rocks and the agreement of these with other estimates of the age of the oldest rocks seem to indicate that the age of the earth is at least 2×10^9 years and no fission process with a half-life less than 5×10^9 years occurs, unless uranium and thorium have been or are now being generated by some terrestrial process."

The events which produced nuclear transformation of an explosive character occurred in the summer of 1945 in Hiroshima and Nagasaki, and the outcome seemed to indicate that the fear expressed earlier by Aston and Joliot was unfounded. The war ended abruptly in Japan's unconditional surrender. Although Japanese were not allowed to continue their studies in nuclear physics and nuclear chemistry, I spent much of my time in the American Library, which was established in downtown Tokyo, reading the post-war scientific journals, which arrived from the United States. A paper written by Seaborg and Perlman⁵ particularly attracted my attention. This paper was mailed as a secret report from Berkeley, Calif., to the "Uranium Committee" in Washington, D.C., on April 13, 1942, and was published in *Journal of the American Chemical Society* 6 years later in 1948.

According to Seaborg and Perlman, a sample of pitchblende from the Great Bear Lake region of Canada contained 1 part of ^{239}Pu in 10^{14} in the original pitchblende concentrate. The plutonium found in pitchblende was the same as that used in the Nagasaki bomb. Neutrons from spontaneous fission of ^{238}U , (α, n) reactions, and cosmic-ray neutrons contribute to the production of 24000-year ^{239}Pu in the following manner:



It appeared to me that the natural occurrence of ^{239}Pu in uranium ores was proof that subcritical uranium chain reactions are actually occurring in nature. Would it not be possible then that the "disparities" such as envisioned by Libby might still be observed if self-sustaining uranium chain reactions had occurred in nature during the geological history of the earth?

Natural Nuclear Reactors

On December 2, 1942, man achieved here the first self-sustaining chain reaction and thereby initiated the controlled release of nuclear energy—so reads the plaque at football stadium of the University of Chicago. In 1957, Donald J. Hughes wrote in his book "On Nuclear Energy": "As an illustration of the awesome nature of these first glimpses of the possibilities, it is interesting to recall that the argument was advanced by some scientists in the early days that the chain reaction would be impossible. They reached this conclusion on the basis that if it really were possible it would have already taken place naturally somewhere in the earth's surface, with disastrous results. To these people it just didn't seem possible that the large-scale release of nuclear energy, so tremendous in comprehension, could be accomplished by the limited efforts of men."

So far I have not been able to identify the scientists who felt that if the chain reaction were really possible

it would have already taken place naturally *somewhere* in the earth's surface. At any rate, the idea of naturally occurring self-sustaining nuclear chain reactions became quite unpopular during the 1950s and remained so for many years. Thus two decades later, in the July 1976 issue of *Scientific American*, George A. Cowan wrote: "The announcement of the Oklo reactor was received by American nuclear scientists with skepticism. Some of the world's best physicists had constructed the Stagg Field reactor with careful attention to mechanical detail, to the purity of the materials and to the geometry of the assembly. Could nature have achieved the same result so casually? We now know that the answer is yes."

The reason why the idea of natural reactors was unpopular during the 1950s was that it appeared that Fermi's pile theory, when applied to uranium ore deposits, lead to an unequivocal conclusion that the chain reaction could never have become self-sustaining. The fact that it is not so was pointed out in a brief article entitled "On the Nuclear Physical Stability of the Uranium Minerals".⁶ In this paper,⁶ I stated: "The infinite multiplication constant, k_∞ , may be considered as an indicator of the stability of the uranium minerals, which are the natural assemblages of uranium, moderator, and impurities. We may consider a system to be quite 'stable', when the infinite multiplication constant of the assemblage is far less than unity. The system will be nuclear physically 'unstable', when the infinite multiplication constant is greater than unity."

According to Fermi's pile theory⁷

$$k_\infty = \epsilon p f \eta$$

where ϵ is the fast fission factor, p is the resonance escape probability, f is the thermal utilization factor, and η is the number of fast neutrons available per neutron absorbed by uranium. When dealing with geological events, the change of the uranium enrichment as a function of geological time should also be taken into consideration. The major neutron sources in minerals are the spontaneous fission and the α, n reactions.

The values of p and f can be calculated if the chemical composition of the mineral is given, ϵ is always close to unity, and η as a function of the uranium enrichment is known. Hence the value of k_∞ of a mineral at any geological time can be calculated.

In the 1956 paper, I chose as an example a pitchblende ore from Johanngeorgenstadt, Saxony, for the calculation of the values of ϵ , p , f , η , and k_∞ . The reason for choosing this pitchblende was twofold: (a) it appeared to be free of the neutron-consuming rare earths, which meant that this ore was likely to be the one which would have most easily become nuclear physically "unstable" during the geological history of the earth; and (b) the chemical analysis of this pitchblende was performed in the 1880s by W. F. Hillebrand of the U.S. Geological Survey, whom I considered as being the greatest analytical chemist of the 19th century. Table I shows the chemical composition of the Johanngeorgenstadt pitchblende.

The values of ϵ , p , f , η , and k_∞ thus calculated as a function of geological time are shown in Table II. Similar calculation showed that none of the uranium minerals was nuclear physically "unstable" during the

(6) P. K. Kuroda, *J. Chem. Phys.*, **25**, 781 (1956).

(7) E. Fermi, *Science*, **105**, 27 (1947).

(5) G. T. Seaborg and M. L. Perlman, *J. Am. Chem. Soc.*, **70**, 1571 (1948).

Table I
Analysis of Johanngeorgenstadt, Saxony, Pitchblende^a

UO ₃	22.33	CaO	1.00
UO ₂	59.30	MgO	0.17
ThO ₂	none	Bi ₂ O ₃	0.75
CeO ₂	none	V ₂ O ₅ , MoO ₃ , WO ₃	0.75
ZrO ₂	none	Alkalies	0.31
(La,Di) ₂ O ₃	none	SO ₃	0.19
(Yt,Er) ₂ O ₃	none	P ₂ O ₅	0.06
Al ₂ O ₃	0.20	As ₂ O ₅	2.34
Fe ₂ O ₃	0.21	He	trace
PbO	6.39	H ₂ O	3.17
CuO	0.17	SiO ₂	0.50
MnO	0.09	Total	97.93

^a Analyst: W. F. Hillebrand (*Bull. U.S. Geol. Surv.*, No. 78, 43 (1891), No. 90, 23 (1892); No. 220, 111-114 (1903)). See also F. W. Clarke, "The Data of Geochemistry", Government Printing Office, Washington, D.C., 1924, 725.

Table II
Value of k_{∞} for a Johanngeorgenstadt Pitchblende as a Function of Geological Time^a

geological time (10 ⁶ years ago)	0 (pre- sent)	700	1000	1400	2100	2800
²³⁵ U enrichment, %	0.7	1.3	1.6	2.3	4.0	7.0
p	0.47	0.45	0.43	0.42	0.38	0.34
f	0.93	0.95	0.96	0.97	0.98	0.99
η	1.32	1.57	1.66	1.77	1.91	1.98
k_{∞}	0.58	0.67	0.69	0.72	0.71	0.67

past 2800 million years: moving back in time the values of f and η steadily increased as the ²³⁵U content increased, but the value of p decreased so the k_{∞} also decreased after reaching a maximum value sometime 1 to 2 billion years ago. The results of these calculations thus seemed to lead to an unequivocal conclusion that the chain reaction could never have become self-sustaining throughout the entire geological history of the earth.

The above calculation was based upon an overly simplified model, however, in which it was assumed that an ore deposit was somehow instantaneously created in nature essentially in its present chemical state. I therefore argued that uranium ores should be treated as assemblages of enriched uranium (fuel), water (moderator), and neutron-absorbing impurities, in which the ratio (n) of water to uranium should be regarded as a variable. In Table II, a slight increase of the water to uranium ratio could have easily caused a sharp upward change of p without affecting f considerably, the result of which could have been enough to make the system nuclear physically "unstable".

I therefore considered that the formation of uranium ores represented the following sequence of events: an aqueous solution of uranium (²³⁵U enriched) is gradually converted to an assemblage of uranium plus n mol of water ($n = 1, 2, 3, \dots, n$) and finally to an almost water-free uranium mineral.

Assuming the Johanngeorgenstadt pitchblende formed 2100 million years ago, I calculated the values of p , f , η , and k_{∞} as a function of n , as shown in Table III. The results indicated that the system could have easily become nuclear physically "unstable" if the size of the assemblage was greater than, say, a thickness of a few feet.

Although these calculations clearly demonstrated that nuclear reactors could have existed in nature during the

Table III
Water-Uranium Ratio (n) and Values of p , f , η , and k_{∞} for a Johanngeorgenstadt Pitchblende, 2100 Million Years Ago^a

n	1/4	1/2	1	2	3	4	5	10
p	0.29	0.47	0.62	0.74	0.79	0.82	0.84	0.86
f	0.99	0.98	0.97	0.95	0.93	0.91	0.89	0.81
η	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91
k_{∞}	0.55	0.88	1.15	1.34	1.40	1.42	1.43	1.33

geological history of the earth, my idea was generally considered as being a mere speculation. The scientists in the 1950s firmly believed in the constancy of the ²³⁸U/²³⁵U ratio in nature. Although there were only few published data on the ²³⁸U/²³⁵U ratios in uranium ores from different localities of the world, they were led to believe that thousands of classified data on the isotopic compositions of uranium were in existence *somewhere* in government laboratories.

At about the same time that my paper appeared, research workers of the French Atomic Energy Commission were finding a new uranium ore deposit at Oklo, now in the Republic of Gabon, Africa. It so happened that the uranium ore from Oklo bore experimental evidence needed for the verification of my theory. Had representative uranium specimens from Oklo been carefully examined mass spectrometrically at that time, an anomaly in the isotopic composition of uranium indicating a depletion of ²³⁵U in the ores would certainly have been noted.

However, it was 16 years later, in 1972, that such an anomaly was actually detected by French investigators. On Sept 25, 1972, the world's scientific community learned of an extraordinary discovery made by research workers of the French Atomic Energy Commission: uranium had been found, in the deposit at Oklo in the Republic of Gabon, Africa, with an abnormal isotopic composition that led one to arrive at the conclusion that self-sustaining nuclear chain reactions had occurred in the remote past. The reaction site consisted of several bodies of very rich uranium ore, and more than 500 tons of uranium had been involved in the reactions with a quantity of energy released equal to about 100×10^9 kW·h. The integrated neutron flux at certain points exceeded 1.5×10^{21} n/cm², and samples have been found in which the concentration of the isotope ²³⁵U was as low as 0.29%, as compared with 0.72% in natural uranium. These results were reported in *Comptes Rendus Hebdomadaires Seances Academie des Sciences* by three groups of French researchers: Bodu et al.,⁸ Neuilly et al.,⁹ and Baudin et al.¹⁰ Table IV shows a part of the experimental data obtained by Neuilly et al.

Until recently, scientists believed that the elements were created only in stars, but the discovery of the Oklo phenomenon revealed the fact that a *nuclear fire* had existed on the earth billions of years ago. Further investigations on the remains of such a nuclear fire seem to hold a key to the solution of one of the most critical problems confronting the human race today: *How to deal with the harmful ashes from the nuclear fire*

(8) R. Bodu, H. Bouzigues, N. Morin, and J. P. Pfiffelmann, *C. R. Hebd. Seances Acad. Sci., Ser. D*, 275, 1731 (1972).

(9) M. Neuilly, J. Bussac, C. Fréjacques, G. Nief, G. Vendryes, and J. Yvon, *C. R. Hebd. Seances Acad. Sci., Ser. D*, 275, 1847 (1972).

(10) G. Baudin, C. Blain, R. Hagemann, M. Kremer, M. Lucas, L. Merlivat, R. Molina, G. Nief, F. Prost-Marechal, F. Regnaud, and E. Roth, *C. R. Hebd. Seances Acad. Sci., Ser. D*, 275, 2291 (1972).

Table IV
Isotopic Anomalies Observed in Uranium Ores from Oklo, in the Republic of Gabon, Africa^a

	Oklo-M	Oklo-310	natural	Oklo-M ^a	Oklo-310 ^a	²³⁵ U fission
²³⁵ U	0.4400 ± 0.0005	0.592 ± 0.001	0.7202			
¹⁴² Nd	1.38	5.49	27.11	0	0	0
¹⁴³ Nd	22.1	23.0	12.17	22.6	25.7	28.8
¹⁴⁴ Nd	32.0	28.2	23.85	32.4	29.3	26.5
¹⁴⁵ Nd	17.5	16.3	8.30	18.05	18.4	18.9
¹⁴⁶ Nd	15.6	15.4	17.22	15.55	14.9	14.4
¹⁴⁸ Nd	8.01	7.70	5.73	8.13	8.20	8.26
¹⁵⁰ Nd	3.40	3.90	5.62	3.28	3.46	3.12

^a Corrected for the part due to the natural element.

Table V
Sequence of Events in the History of the Earth

event	time (years ago)
oldest rocks on earth	3.5 billion
oldest fossils	3.4 billion
oceans formed	3.0 billion
plants began oxygen production	2.0 billion
natural reactors formed	1.7 billion
atmosphere formed as now known	1.0 billion

created by 20th century man? The International Atomic Energy Agency thus felt that the Oklo phenomenon was an excellent subject for international cooperation on fundamental research and welcomed the proposal made by the Government of Gabon and the French Atomic Energy Commission to hold a symposium,¹¹ only 3 years after the discovery was made.

An excellent review article entitled "Fossil Nuclear Reactors" has recently been published by Michel Maurette.¹² Although no attempt will be made here to discuss the results obtained from the recent investigations on the Oklo phenomenon, it is interesting to point out that the formation of natural reactors is closely related to the appearance of life on our planet Earth. According to Maurette, the high uranium concentrations found at Oklo are end products of a long chain of repetitive fractionation processes where oxygen played a dominant role as an oxidizing agent. It is generally assumed that this element was injected only 2×10^9 years ago into the earth's atmosphere by a new generation of living organisms. Consequently the high uranium concentration required for triggering nuclear chain reaction was probably never achieved in uranium-ore deposits older than 2×10^9 years, and the occurrence of fossil nuclear reactors was probably limited to a relatively narrow period of time ranging from about 1 to 2×10^9 years ago, as shown in Table V.

Plutonium-244 in the Early Solar System

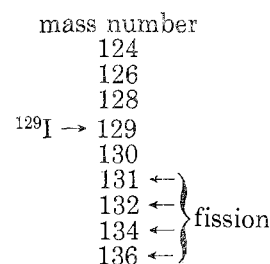
In 1951 the long-lived isotope of iodine, ¹²⁹I, which β -decays into the stable ¹²⁹Xe, was discovered.¹³ The half-life of ¹²⁹I, 1.7×10^7 years, is comparable to the time interval between the formation of the elements in stars and the birth of the earth. If ¹²⁷I and ¹²⁹I were created in stars in approximately equal quantities, the radioactive ¹²⁹I could have decayed away completely by now, since its half-life is much shorter than the age of the earth. Thus it appeared as if the disappearance of ¹²⁹I may explain the fact that the atomic weight of iodine (126.9) is now smaller than that of tellurium (127.60).

(11) "The Oklo Phenomenon", Proceedings of a Symposium, Libreville, 23-27 June 1975, International Atomic Energy Agency, Vienna, 1975.

(12) Michel Maurette, *Annu. Rev. Nucl. Sci.*, **26**, 319 (1976).

(13) S. Katcoff, O. A. Schaeffer, and J. M. Hastings, *Phys. Rev.*, **82**, 688 (1951).

Such a process, however, would produce an effect of decreasing the atomic weight of xenon (131.30) by enriching the relative abundance of ¹²⁹Xe. In order to counterbalance such an effect, I felt that it was necessary to consider the possibility that xenon may have become "heavier" because of the addition of the heavy isotopes ¹³¹⁻¹³⁶Xe produced by the process of fission:



There appeared to be two possibilities: (a) self-sustaining uranium chain reactions could have occurred on the earth and/or (b) some unknown transuranium elements could have decayed by spontaneous fission during the early history of the earth. I discussed these possibilities in two papers published in 1956⁶ and 1960,¹⁴ respectively.

In regard to possibility b that some transuranium elements might have decayed by spontaneous fission during the early history of the earth, Seaborg and his co-workers,¹⁵ in 1951, were aware of the fact that one of the yet-to-be discovered isotopes of element 94, ²⁴⁴Pu, may have a half-life as long as 100 million years, and if so, it may still remain on the earth. A search for ²⁴⁴Pu in several uranium, thorium, and rare earth minerals was therefore carried out, but none contained a detectable quantity of this nuclide.

In 1954 the long-lived isotope of plutonium was discovered in the debris from the November 1952 thermonuclear test conducted in the South Pacific.¹⁶ The half-life of the newly discovered ²⁴⁴Pu turned out to be 82 million years or $1/56$ th of the age of the earth, which is now thought to be 4.6 billion years. Thus it became apparent by the middle of the 1950s that the primordial ²⁴⁴Pu had decayed to an almost infinitesimal fraction of its initial abundance and hence it would be futile to attempt to detect it on the earth today.

A paper entitled "Californium-254 and Supernovae" by Burbidge and co-workers¹⁷ appeared in 1956; they suggested that the spontaneous fission of ²⁵⁴Cf with a half-life of 55 days may be responsible for the form of

(14) P. K. Kuroda, *Nature (London)*, **187**, 36 (1960).

(15) C. A. Levine and G. T. Seaborg, *J. Am. Chem. Soc.*, **73**, 3278 (1951).

(16) M. H. Studier, P. R. Fields, P. H. Sellers, A. M. Friedman, C. M. Stevens, J. F. Mech, H. Diamond, J. Sedlet, and J. R. Huizenga, *Phys. Rev.*, **93**, 1433 (1954).

(17) G. R. Burbidge, F. Hoyle, E. M. Burbidge, R. F. Christy, and W. A. Fowler, *Phys. Rev.*, **103**, 1145 (1956).

the decay light curves of supernovae of type I which have an exponential form with a half-life of 55 nights. According to these astrophysicists, the presence of Tc in red giant stars and of Cf in type II supernovae appeared to be observational evidence that neutron capture processes on both a slow and a fast time scale have been necessary to synthesize the heavy element in their observed cosmic abundances.

Meanwhile, one day during the winter of 1957–58, A. H. W. Aten, Jr., of the Instituut voor Kernphysisch Onderzoek in Amsterdam visited the Argonne National Laboratory and gave a seminar. I attended the lecture and listened to what Aten had to say then about the “age” of the elements.¹⁸

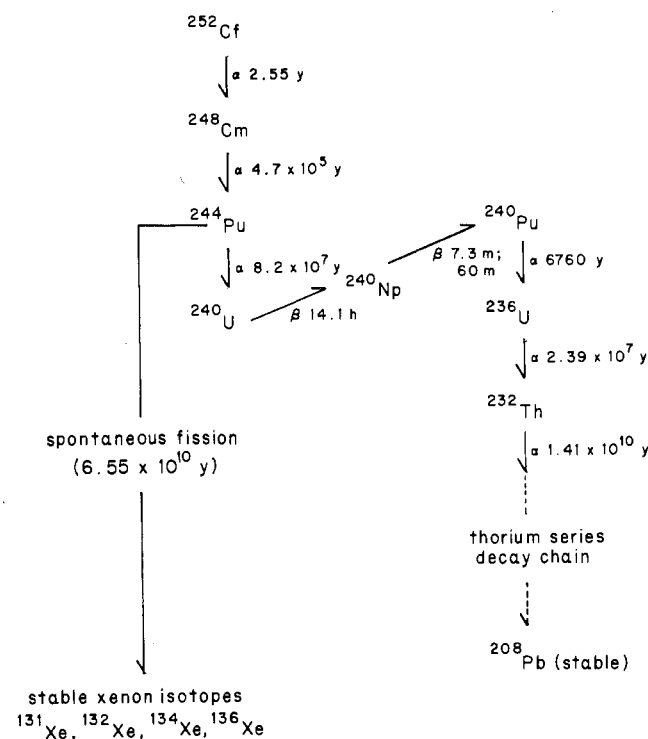
Aten distinguished four phases in the formation of transuranic nuclei which today exist as uranium and thorium. In the first stage nuclei were formed, many of which had an appreciable neutron excess. These are called the “original” nuclei. During the succeeding period these nuclei changed into β -stable isobars by means of β decay. The quantities which existed after β stabilization are called “stabilized” quantities. Now the “fast” α processes set in; these were much slower than the β decays, but much faster than the “slow” α decay of ^{238}U , ^{235}U , and ^{232}Th . During this period the decay of ^{238}U , ^{235}U , and ^{232}Th has been negligible. Some of these fast α processes were followed by even faster β decays, and the final products formed were ^{238}U , ^{235}U , and ^{232}Th . Both the first and the second period were very short compared to the total present age of the elements, and it appears as if we are fully justified in neglecting their duration. At this point, however, Aten added the following remark: *The slowest of the “fast” α decays, that of ^{244}Pu , might have played a small role if it had not been for the fact that only a relatively small fraction of the present ^{232}Th has come from or passed through this nuclide.*

I thought that the remark made by Aten was very interesting. It appeared to me that a significant amount of ^{244}Pu must have existed in nature shortly after the earth was formed and, if so, it may have partially decayed by spontaneous fission to produce the heavy xenon isotopes in the earth’s atmosphere (Scheme I).

To test this idea, it was only necessary to compare the isotopic composition of the xenon in the earth atmosphere with that of the xenon in extraterrestrial samples such as meteorites. The rare-gas mass spectrometer, which enables one to perform such an experiment, was just being constructed at about this time by John H. Reynolds¹⁹ at the Department of Physics of the University of California at Berkeley. It was 3 years later in 1960 that Reynolds made the important discovery that the xenon extracted from the meteorite Richardton was highly enriched in ^{129}Xe ; he attributed this enrichment to the decay of $17 \times 10^6 \text{ y } ^{129}\text{I}$ during the early history of the solar system.

If $17 \times 10^6 \text{ y } ^{129}\text{I}$ existed in the early solar system, $82 \times 10^6 \text{ y } ^{244}\text{Pu}$ should have been also present in the early solar system, and the xenon extracted from the meteorite should have been enriched in the heavy isotopes of xenon. When the isotopic composition of xenon in Richardton meteorite was compared with that of the atmospheric xenon, however, it was found exactly the

Scheme I



opposite to be the case: ^{129}Xe was enriched, but $^{131-136}\text{Xe}$ were depleted in the meteorite relative to the xenon in the atmosphere. Thus the results obtained by Reynolds appeared to indicate that ^{244}Pu did not exist in nature in the early solar system. This would have been too hasty a conclusion, however. I argued instead for the existence of ^{244}Pu in the early solar system in a paper entitled “Nuclear Fission in the Early History of the Earth”, which appeared in the July 2, 1960, issue of *Nature*.¹⁴

Since I put forward the hypothesis in 1960 that extinct ^{244}Pu spontaneous fission may be responsible for the general Xe anomalies in the mass region 131–136, several instances have been reported of the earth’s atmosphere being enriched in the heavier Xe isotopes relative to meteorites. However, no clear-cut evidence had been obtained previously for fission-produced $^{131-136}\text{Xe}$ in meteorites, as would be expected from the theory in high U–Th/low primordial Xe meteorites, until Marvin W. Rowe, now at the Texas A&M University, joined my group as a graduate student in 1963. Rowe then decided to search for evidence of fission xenon in the high U–Th meteorites. Several meteorites with unusually high Th contents were chosen to be examined. The first sample of this group which was measured, a 4.45-g piece of the Pasamonte eucrite, did indeed contain fissionogenic xenon,²⁰ as shown in Table VI.

A vast amount of supporting evidence for the existence of ^{244}Pu in the early solar system have since been accumulated. The first to be reported were excess fossil fission tracks produced by ^{244}Pu in the meteorites Moore County and Toluca.²¹ The final evidence that the fission xenon found in the meteorites was in fact the spontaneous fission decay products of ^{244}Pu was

(20) M. W. Rowe and P. K. Kuroda, *J. Geophys. Res.*, **70**, 709 (1965).

(21) R. L. Fleischer, P. B. Price, and R. M. Walker, *J. Geophys. Res.*, **70**, 2703 (1965).

(18) A. H. W. Aten, Jr., *Physica*, **23**, 1073 (1957).

(19) J. H. Reynolds, *Phys. Rev. Lett.*, **4**, 8 (1960).

Table VI
Fissiogenic Xenon from the Pasamonte Meteorite²⁰

ⁱ Xe/ ¹³⁰ Xe, i =	Pasamonte	average carbonaceous chondrites ^a	atmos- phere ^b
128	0.59 ± 0.01	0.52	0.47
129	6.45 ± 0.08	6.48 ^c	6.48
130	≡1.00	≡1.00	≡1.00
131	5.22 ± 0.06	5.08	5.19
132	6.85 ± 0.07	6.23	6.59
134	3.26 ± 0.02	2.36	2.56
136	2.92 ± 0.02	2.00	2.17

$$^{130}\text{Xe} = 0.35 \times 10^{-11} \text{ cm}^3 \text{ STP/g.}$$

^a D. Krummenacher et al., *Geochim. Cosmochim. Acta*, **26**, 231-251 (1962). ^b A. O. Nier, *Phys. Rev.*, **79**, 450-454 (1950). ^c Value for Murray only.

reported²² by Alexander and co-workers in 1971. They used 13.0 mg of "pure" ²⁴⁴Pu (as PuO₂) and measured the relative yields of the fissiogenic xenon isotopes mass spectrometrically. They showed that the results agreed almost perfectly with the mass yields deduced from the meteorite xenon data.

It is important to note here that ²⁴⁴Pu is not completely extinct on the earth today, as it can be shown by the following calculation: Let the ²⁴⁴Pu/²³⁸U ratio 4.6 billion years ago be x . Then the same ratio today is $(1/2)^{56} \times x = 3 \times 10^{-17} \times x$. The total mass of the earth equals 5.977×10^{27} g, and we may assume the average uranium content of the earth to be the same as that in chondrites (10 ppb). Thus the total amount of uranium in the earth is 6×10^{19} g. Hence the total amount of ²⁴⁴Pu remaining on the earth today must be about $1800x$ g.

The value of x can be obtained from the observed ^{136f}Xe/²³⁸U ratio in meteorites. According to Rowe and

(22) E. C. Alexander, Jr., R. S. Lewis, J. H. Reynolds, and M. C. Michel, *Science*, **172**, 837 (1971).

Kuroda,²⁰ ^{136f}Xe in the meteorite Pasamonte is $3.2 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$ and the uranium content is 54 ppb. A simple calculation yields a value of $x = 0.004$, and hence the total amount of the primordial ²⁴⁴Pu remaining on the earth today is about $(1800)(0.004) = 7$ g.

The total inventory of man-made ²⁴⁴Pu in the world today is not known, but it is likely to be not much greater than the amount of primordial ²⁴⁴Pu remaining on the earth. Attempts have been made by a number of investigators to detect the primordial ²⁴⁴Pu in terrestrial minerals, but the results obtained so far appear to be inconclusive.

Concluding Remarks

A brief account of the investigations on the occurrences of the natural reactor and ²⁴⁴Pu in the early history of the earth and the solar system, respectively, has been presented. Although a number of reports on the natural occurrence of "super-heavy" elements have appeared in recent years, none of the experimental evidence presented so far turned out to be conclusive.²³ Plutonium-244 thus remains the only nuclide heavier than uranium whose existence in the early solar system has been firmly established, while the Oklo reactor remains today as the only natural nuclear reactor so far found in the world.

I wish to express my deep appreciation to the U.S. Atomic Energy Commission and the National Science Foundation for the support of these investigations, and to my former Ph.D. students, especially to those participating in the Award Symposium held in Anaheim, Calif., during March 14-16, 1978.

(23) See, for example, R. V. Gentry, T. A. Cahill, N. R. Fletcher, H. C. Kaufmann, L. R. Medsker, J. W. Nelson, and R. G. Flochini, *Phys. Rev. Lett.*, **37**, 11 (1976); E. Anders, H. Higuchi, J. Gros, H. Takahashi, and J. W. Morgan, *Science*, **190**, 1262 (1975); O. K. Manuel, D. D. Sabu, R. S. Lewis, B. Srinivasan, and E. Anders, *ibid.*, **195**, 208 (1977).