Plutonium anomaly in nature

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(Received September 26, 1983; Accepted February 28, 1984)

The $^{239}\text{Pu}/^{238}\text{U}$ ratios are reexamined in volcanic ashes and rock, uranium mineral and other contemporary terrestrial samples and also in the atmospheric samples. This ratio in rain samples collected at Fayetteville (36°N, 94°W), Arkansas, reaches up to 10^{-5} (atom/atom), which is about 2 orders of magnitude higher than those of volcanic ashes and rock and about five or six orders of magnitude higher than the $^{239}\text{Pu}/^{238}\text{U}$ ratio of 10^{-12} (atom/atom) typical of uranium minerals. The data obtained from our measurements indicate that the high $^{239}\text{Pu}/^{238}\text{U}$ ratios observed in this contemporary terrestrial samples are due to fallout contaminations.

INTRODUCTION

The fact that extremely small quantities of ^{239}Pu occur in uranium-bearing minerals was first reported by SEABORG and PERLMAN (1948). According to LEVING and SEABORG (1951), the $^{239}\text{Pu}/^{238}\text{U}$ ratios in three samples of pitchblende ranged from 7.1 to 12×10^{-12} (atom/atom). The occurrence of ^{244}Pu in the early history of the solar system was established in our laboratories during the 1960's (KURODA, 1960; KURODA, 1961; ROWE and KURODA, 1965). The $^{244}\text{Pu}/^{238}\text{U}$ ratio in nature at the time of formation of the early solar system is known to be on the order of 10^{-2} (atom/atom) (KURODA, 1961; PODOSEK, 1970; PODOSEK and LEWIS, 1972; KURODA, 1982), while the total amount of the primordial ^{244}Pu still remaining on the earth today was estimated to be roughly 7 grams (KURODA, 1982). Attempts have been made by a number of investigators to detect the primordial ^{244}Pu in terrestrial minerals, but the results obtained so far appear to be negative or inconclusive (FIELDS *et al.*, 1966; HOFFMAN *et al.*, 1971). It is worthy of note here that the abundance of ^{239}Pu relative to ^{238}U in the Oklo deposit, when it was in operation about 2 billion years ago, was similar to that of ^{244}Pu relative to ^{238}U at the time of

formation of the solar system. According to HAGEMANN *et al.* (1975), fission products found in the Oklo reactor are mixtures of the products of ^{235}U , ^{238}U and ^{239}Pu fission in the ratio of 93 percent, 3 percent and 4 percent, respectively (see also, KURODA, 1982). This means that ^{239}Pu once existed in nature in far greater quantities than the amounts found in uranium-bearing minerals and rocks today.

It has been reported by a number of investigators, however, that plutonium is highly enriched relative to uranium in volcanic rocks, tufas and thermal waters. CHERDYNTSEV *et al.* (1968) have reported that the $^{239}\text{Pu}/^{238}\text{U}$ ratios reached 1.7×10^{-5} (atom/atom) for a sample of limonite from the fumarole field in Kamchatka and 1.8×10^{-6} (atom/atom) in a sample of volcanic bomb from the volcanic region of Caucasus. They also found that the $^{239}\text{Pu}/^{238}\text{U}$ ratio in a sample of water from the fumarole field of Kamchatka was also as high as 1.3×10^{-6} (atom/atom) and suggested that these abnormal enrichments of ^{239}Pu relative to ^{238}U were probably due to existence of an unknown transuranium element in nature, which decays into ^{239}Pu . PRASOLOV (1974) then put forward the hypothesis that these isotopic anomalies may be attributable to the Oklo phenomenon, which is still occurring inside the earth's crust

today.

The fact that ^{239}Pu is highly enriched relative to ^{238}U in volcanic samples was confirmed by MEIER *et al.* (1974), who found that the $^{239}\text{Pu}/^{238}\text{U}$ ratios in various samples from different locations and eruptions reached values up to 10^{-7} (atom/atom), several orders of magnitude higher than the values of 10^{-11} (atom/atom), which is typical for uranium minerals. They reported that a contamination by ^{239}Pu from fall-out was out of the question and suggested that either the Oklo phenomenon or the existence of an unknown super-heavy element was the likely cause of the isotopic anomalies observed in plutonium.

In this paper, the authors intend to report the set of data for the $^{239,240}\text{Pu}/^{238}\text{U}$ (atom/atom) ratios obtained from the study of these two radionuclides in the atmosphere and contemporary terrestrial samples, in order to show that the anomaly of plutonium isotope in nature is due to fallout contamination.

EXPERIMENTAL

Water samples: The rain and snow samples were collected on the roof of the Chemistry Building of the University of Arkansas, Fayetteville (36°N , 96°W), Arkansas. A large volume of rainwater (about 100ℓ) was collected after each rain and it was acidified to $\text{pH} \sim 2$ in the laboratory. The rainwater sample was then spiked with one or two ml each of ^{232}U and ^{242}Pu tracers and coprecipitated with iron hydroxide at pH 9-10. The supernate was siphoned off and the precipitate was collected for analysis. After acid treatments with HNO_3 , HClO_4 , and HF , the solution was made into 8M HNO_3 .

A large volume of water samples (about 100ℓ) from Hot Springs, Arkansas, was treated exactly as described above. The samples were brought to the laboratory in 20-l polythene bottles for the analysis.

Soils: The soil samples from the University of Arkansas were collected in an open area quite close to our laboratory, where a new

engineering building is under construction. The sampling was done at different depths ranging from the top soil to 4.5M deep. The forest soil samples were supplied by PAUL M. KURODA of the Agronomy Department of the University of Arkansas. The method of preparation and analysis of the soil samples was the same as the one described by CHU (1971), which involved leaching with nitric acid and hydrochloric acid followed by ignition of the residue in a platinum crucible and digested with hydrofluoric acid. The final solution then made into 8M HNO_3 . Up to 100g each of soil samples was used for analysis.

Volcanic ashes and rocks: The volcanic ash from Mount St. Helens eruption was collected at Morton, Washington, off a cement surface, a 3/4 inch layer of ash under a woven wire fence at a lumber yard. The town is 20 miles North and about 2 miles West of Mount St. Helens. The volcanic ash from Portland, Oregon, was hosed off from the roof of a building, two weeks after the eruption of Mount St. Helens. Both samples were supplied to our laboratory by Arthur Fry of the University of Arkansas, Fayetteville.

About 12 grams of each sample was used for analysis, by digesting the fine powder with nitric acid and perchloric acid; and the residue made into 8M HNO_3 .

The volcanic rock sample was collected by KIMIO NOGUCHI and one of us (P.K. KURODA) from Mihara volcano in Japan and brought to the laboratory for analysis. About 50g of the ground powder was treated similar to the soil samples described above.

Tufas: The tufa sample from Masutomi, Japan, was collected by KIMIO NOGUCHI and one of us (P.K. KURODA), while the Hot Spring tufas from Arkansas were collected by one of us (P.K. KURODA) in the early 1950's.

These samples dissolved very easily in nitric acid solution. About 10–50g was used for each analysis and the solution was made into 8M HNO_3 .

Separation of uranium and plutonium fractions from each sample was carried out

according to the method described by BISHOP *et al.* (1978). The solution in 8M HNO₃ was passed through an anion exchange column (AG 1 × 8, 100–200 mesh, 10ml). Plutonium fractions were eluted from the column with a solution of conc. HCl containing 1M NH₄ I. Uranium fractions were eluted from the same column with 8M HNO₃ solution.

Purification of each fraction was then carried out by extracting uranium fractions with ethyl acetate and further passing the solution through a mini anion exchange column (AG 1 × 8, 100–200 mesh, 1ml), while plutonium fraction was extracted with triisooctylamine (TIOA) in xylene. The purified uranium and plutonium fractions were electrodeposited on a steel planchet according to the method of TALVITIE (1972); and alpha counted with a dual (ORTEC-576) alpha spectrometer with silicon surface barrier detectors.

The control experiments carried out in our laboratory by one of us (I.O. ESSIEEN) have already been described (see SAKURAGI *et al.*, 1983).

RESULTS AND DISCUSSION

Results from the measurement of plutonium and uranium isotopes in rain and snow samples in our laboratory for the period between March 1980 through May 1981 have already been published (SAKURAGI *et al.*, 1983). Uranium-234 and U-235 were found to be highly enriched relative to U-238 in several rain samples collected at Fayetteville (36°N, 94°W), Arkansas, during the months of April and May of 1980. This anomalous uranium was attributed to the burnup of the Soviet Satellite, Cosmos-954.

The uranium fallout occurred just about the time Mount St. Helens erupted on May 18, 1980. In our recent report (KURODA *et al.*, 1983), we have been able to show that a large amount of natural uranium was injected into the atmosphere by the eruption of Mount St. Helens.

SAKURAGI *et al.* (1983), also noted that the concentration of ²³⁸Pu and ^{239,240}Pu in rain at

Fayetteville, Arkansas, increased during the summer months of 1980, after the eruption of Mount St. Helens. Figure 1 shows the plot of ^{239,240}Pu/²³⁸U versus ²³⁸U concentration in rain collected at Fayetteville, Arkansas, during the period from March 1980 to May 1981. It is interesting to note here that an inverse relationship seems to occur between ^{239,240}Pu/²³⁸U ratios and the concentrations of ²³⁸U: The higher the concentration of ²³⁸U in rain, the lower the ^{239,240}Pu/²³⁸U ratios. A similar relationship has also been noticed in most of the rain and snow samples collected at Fayetteville, Arkansas, during the period of June 1981 to April 1982 (ESSIEEN, 1983). Recently, HIROSE and SUGMURA (1983), reported that the concentration of plutonium in the surface air in Japan increased abruptly from March through June of 1981 with a maximum value of 21.4 a Ci m⁻³ in June of 1981.

Fig. 1 The activity ratios of ^{239,240}Pu/²³⁸U versus ²³⁸U concentration in rain at Fayetteville, Arkansas, during the period from March 1980 to May 1981.

These results seems to indicate that there was probably a significant inventory of more ^{239}Pu into the atmosphere by the eruption of Mount St. Helens or by the recent Chinese test of October 16, 1980. Nevertheless, in most of the rain samples, the $^{239,240}\text{Pu}/^{238}\text{U}$ (atom/atom) ratios reached up to 10^{-5} , several orders of magnitude higher than the value of 10^{-12} , which is typical of uranium minerals.

Since it has been found that the $^{239,240}\text{Pu}/^{238}\text{U}$ ratio in the atmosphere was higher than the value reported for uranium minerals, it was therefore necessary to examine this ratio in some contemporary terrestrial samples in order to be able to explain such anomaly. The eruption of Mount St. Helens also provided the volcanic ash samples for such measurements and studies. Table 1 shows the results obtained for these terrestrial samples.

Table 1. Uranium and plutonium isotopes in volcanic ashes, tufas, hot springs, rainwater and soils

Samples/Location	Concentrations (in fCi/g or fCi/g)					$^{239}\text{Pu}/^{238}\text{U}$ (atom/atom)
	^{234}U	^{235}U	^{238}U	^{238}Pu	$^{239,240}\text{Pu}$	
Volcanic ashes: Mt. St. Helens						
Morton, Washington	239± 12	11.2±2.0	239± 12	< 1	3.0±1.0	7.1×10^{-8}
*Seattle, Washington	221± 13	9.9±2.0	221± 13	< 1	26 ±7.0	6.6×10^{-7}
*Portland, Oregon	331± 16	18.3±3.2	324± 16	< 1	7.3±2.3	1.3×10^{-7}
Portland, Oregon	43.5± 2	2.1±0.4	38± 1.8	< 1	13.5±1.6	2.0×10^{-6}
Volcanic rock: Mihara Volcano (Japan)	45± 5	2.0±0.6	45± 4	< 0.1	1.9±0.3	2.3×10^{-7}
Hot spring tufas:						
Masutomi (Japan)	100± 14	< 1	105± 15	< 0.1	0.7±0.3	3.8×10^{-8}
Egg spring, Hot springs (Arkansas)	2,335±200	68± 9	1,451±125	< 1	23.7±1.9	8.7×10^{-8}
Old tufa, Hot springs (Arkansas)	30± 2.0	1.1±0.3	21.8± 1.4	< .1	10 ±3.0	2.5×10^{-6}
Hot spring water, Arkansas	2.1± 0.2	0.1±0.03	1.7± 0.1	< 0.01	0.9±0.3	2.9×10^{-6}
Hot spring sediment, Arkansas	400± 22	14.7±1.6	305± 18	1.0±0.2	10.2±0.9	1.8×10^{-7}
Soils: Univ. of Arkansas						
Surface soil	637± 61	21±3.0	532± 51	1.0±0.08	12.9±2.8	1.3×10^{-7}
3.0 meters deep	683± 72	21±3.0	491± 54	0.4±0.1	32 ±1.2	3.5×10^{-7}
4.5 meters deep	300± 18	9.6±1.2	198± 12	1.9±0.4	7.9±1.0	2.2×10^{-7}
Forest soil, Arkansas	461± 37	18.1±2.6	450± 36	1.4±0.3	71 ±4.0	8.7×10^{-7}
Rainwater samples at Fayetteville, Arkansas						
1980						
Mar. 29	8.5± 0.7	0.2±0.1	8.6±0.7	0.13±0.09	2.9±0.5	1.8×10^{-6}
Apr. 16	521± 74	17.2±4.4	36.0±7.3	—	—	—
May 15	188± 18	6.0±1.5	6.3±1.5	0.6±0.3	8.7±0.1	7.8×10^{-6}
May 20 & 22	42.3± 0.3	2.1±0.5	4.6±0.8	0.2±0.1	9.1±0.9	1.3×10^{-6}
May 31	219± 39	11.4±4.1	40.3±9.4	2.1±0.8	99.0±11.0	1.34×10^{-5}
June 17	52.0± 3.7	2.6±0.6	11.4±1.3	0.4±0.3	8.6±1.4	4.1×10^{-6}
June 19	39.2± 3.2	1.5±0.5	11.8±1.4	0.7±0.2	7.2±0.6	3.3×10^{-6}
June 20	23.7± 1.8	1.2±0.3	6.6±0.8	0.4±0.2	5.3±0.6	4.3×10^{-6}
June 22	42.3± 0.3	2.1±0.5	4.6±0.8	0.2±0.1	9.1±0.9	1.1×10^{-5}
June 30	69.0±11.6	2.9±1.6	50.9±9.1	0.6±0.3	16±2	1.7×10^{-6}
July 17	156± 12	6.5±1.6	120± 10	1.1±0.3	24±2	1.1×10^{-6}
July 21	37.0± 2.9	1.5±0.4	29.1±2.4	0.2±0.1	9.1±1.1	1.7×10^{-6}
Aug. (composite)	156± 12	6.5±1.6	120± 10	0.82±0.19	9.4±0.7	4.2×10^{-7}
Sep. 2	166± 15	5.3±2.0	106± 11	1.3±0.6	1812	0.9×10^{-6}
Sep. 16	81.9± 6.9	3.1±0.8	65.8±5.8	0.39±0.02	16±1	1.3×10^{-6}
Sep. 27	30.4± 1.9	1.8±0.4	25.0±1.7	0.9±0.3	14±1	3.0×10^{-6}
Oct. 16	28.1± 2.9	0.9±0.5	20.7±2.4	0.9±0.4	7.6±1.2	2.0×10^{-6}
Oct. 23	20.2± 1.9	0.6±0.3	17.1±1.7	0.9±0.2	8.3±1.0	2.6×10^{-6}
Dec. 26	18.5± 1.8	0.9±0.4	20.8±1.8	1.2±0.5	12±2	3.1×10^{-6}

Table 1. (Continued)

Samples/Location	Concentrations (in fCi/g or fCi/l)					²³⁹ Pu/ ²³⁸ U (atom/atom)
	²³⁴ U	²³⁵ U	²³⁸ U	²³⁸ Pu	^{239,240} Pu	
Rainwater samples at Fayetteville, Arkansas						
1981						
Mar. 3	32.0±4.0	1.6±0.8	28.4±4.0	0.5±0.2	47.6±2.4	0.9 × 10 ⁻⁷
Apr. 28	23.9±1.6	0.6±0.2	24.9±1.6	—	—	—
May 4	14.4±1.6	1.4±0.5	15.5±1.7	1.1±0.5	40.0±2.6	1.3 × 10 ⁻⁵

Concentrations of uranium and plutonium isotopes in volcanic ashes, tufas, hot springs, rainwater and soils; with $^{239,240}\text{Pu}/^{238}\text{U}$ (atom/atom) ratios

Samples of soil at different depths collected near our laboratory were found to have $^{239,240}\text{Pu}/^{238}\text{U}$ (atom/atom) ratios of 10^{-7} , about two orders of magnitude lower than the rain samples and about five orders of magnitude higher than uranium minerals.

The volcanic ash samples collected at different locations after the eruption of Mount St. Helens had a $^{239,240}\text{Pu}/^{238}\text{U}$ ratio ranging from 10^{-6} to 10^{-8} (atom/atom). The difference between this ratio for the ash samples can be explained as due to contamination with small amounts of ^{239}Pu originating from fallout of previous nuclear weapon tests; since the ratios of $^{234}\text{U}/^{238}\text{U}$ were similar to the normal natural ratios of 1.00 (Ci/Ci). It is worthy to note here that the ash samples were collected about two weeks after the eruption and these ash samples were rained on by the sudden subsequent rains just after the eruption, which is the major source of the contamination by ^{239}Pu . Other samples on Table 1 had a $^{239,240}\text{Pu}/^{238}\text{U}$ ratio that fall between 10^{-6} and 10^{-12} (atom/atom).

The volcanic rock from Mihara volcano, Japan, also gave $^{239}\text{Pu}/^{238}\text{U}$ (atom/atom) ratio of 10^{-7} comparable to those found by MEIER *et al.* (1974), in the rock samples from other volcanoes. They reported that samples from different locations and eruptions were found to have uranium contents in the range from 0.1 to 0.2ppm and ^{239}Pu contents of the order of 10^{-14} (g/g) of which the $^{239}\text{Pu}/^{238}\text{U}$ ratios

reached up to 10^{-7} (atom/atom).

The results for the concentration of ^{238}Pu in these terrestrial samples are also presented in Table 1. It is worthy of note that, DAVIS and MEWHERTER (1962) estimated the $^{238}\text{Pu}/^{238}\text{U}$ ratio in Belgium Congo pitchblende to be less than 2.0×10^{-14} (g/g); while $^{239}\text{Pu}/^{238}\text{U}$ ratio was given as 2.8×10^{-12} (g/g). The concentration of ^{238}Pu in pitchblende can thus be estimated to be less than 6.70×10^{-6} fci/g. This means that in uranium minerals, the ^{238}Pu is well below the detection limit if present. As shown in Table 1, detectable concentrations of ^{238}Pu have been found in rainwater, soils and even in Hot Spring sediments. In other samples, like the volcanic ashes, volcanic rock and tufas, the possibility of detecting trace amounts of ^{238}Pu is not completely ruled out. Very large quantities of samples used for analysis may give a positive result. The point to note here is that the $^{238}\text{Pu}/^{239}\text{Pu}$ activity ratios found in most rain samples were equivalent to the ratios in the soil.

Let us examine the main source of plutonium isotopes ($^{239,240}\text{Pu}$ and ^{238}Pu) in our environments. It is generally known that $^{239,240}\text{Pu}$ isotopes are derived from nuclear weapon testing and they accumulate on land through radioactive fallout. The results from the study of $^{239,240}\text{Pu}$ and ^{238}Pu up to the end of 1973 in Tokyo, Japan, for an example, have been reported by MIYAKE *et al.* (1968, 1970, 1975). According to their results, the total

amount of $^{239,240}\text{Pu}$ accumulated on land in Tokyo is estimated to be 1.2mCi/km^2 , with a small amount of ^{238}Pu derived from nuclear detonations and the accidental release of SNAP-9A incident. In a recent report by KATSURAGI *et al.* (1982), on the study of plutonium fallout in Japan, they noted that the highest amount of plutonium deposited on land between 1974 and 1980 was in 1978 ($^{239,240}\text{Pu} = 7.40\mu\text{Ci/km}^2$; $^{238}\text{Pu} = 0.19\mu\text{Ci/km}^2$). For the period of 1958 to 1973 the highest concentration of $^{239,240}\text{Pu}$ deposited was $203\mu\text{Ci/km}^2$ in 1958, which decreased to $37\mu\text{Ci/km}^2$ in 1960 and increased again to $200\mu\text{Ci/km}^2$ in 1963. Their results, however, indicate that the increasing nuclear weapon testings and other man-made sources of plutonium have so much contaminated our earth's surface.

HARDY *et al.* (1973), measured the ^{239}Pu concentration in soils and reported that by the end of 1970 about $13.4 \pm 2.2\text{kCi}$ out of the 17.0kCi of ^{239}Pu originally present in the SNAP-9A generator was deposited on the earth's surface. It is known that the fallout of plutonium is adsorbed on the soil surface layer and is hardly leached out (SAKANOE and TSUI, 1971; MIYAKE *et al.*, 1973; HIROSE and SUGIMURA, 1981). It is therefore reasonable to point out that the $^{239}\text{Pu}/^{238}\text{U}$ ratios of the terrestrial samples can in fact be affected by the input of this artificial plutonium into our environment.

Table 2 shows the concentrations of uranium and plutonium isotopes in a soil sample

collected during the groundbreaking of the Chemistry Building at the University of Arkansas, Fayetteville, in 1933. This soil sample has not been affected by fallout plutonium, since the input of the artificial plutonium into our environment did not occur until the late 1940's. As can be noticed in Table 2, the $^{239}\text{Pu}/^{238}\text{U}$ ratio reported here is less than 1.7×10^{-9} (atom/atom) which may be comparable to the ratio found in uranium minerals. It is also interesting to note that ^{238}Pu was not detected in this soil.

Earlier investigators (CHERDYNTSEV *et al.*, 1968; MEIER *et al.*, 1974) have observed similar variations in plutonium to uranium ratios in volcanic ashes, rocks and uranium containing minerals and they interpreted their results as due to the presence of superheavy nuclides which decays to increase the $^{239}\text{Pu}/^{238}\text{U}$ ratios in these samples compared to uranium minerals. They ruled out the possibility of fallout contamination.

It is worthy of note here that SAKANOE and KOMURA (1971) had found an anomalously high $^{234}\text{U}/^{238}\text{U}$ ratio of about 15 (Ci/Ci) in a maghemite sample from north-east Japan, and they explained this anomalous ^{234}U observed as due to α -recoil of ^{234}U atoms. In comparison, the decay of a superheavy nuclide to ^{239}Pu should have enhanced the $^{239}\text{Pu}/^{238}\text{U}$ ratio more than the 10^{-7} (atom/atom) ratios observed in the volcanic rock, and in the soils if ^{234}U as a results of α -recoil process could enhance the $^{234}\text{U}/^{238}\text{U}$ ratio by a factor of 15 in natural

Table 2. Uranium and plutonium isotopes in the ground breaking soil during the building of the Chemistry Building, University of Arkansas, in 1933

Concentrations (in fCi/g)					$^{239}\text{Pu}/^{238}\text{U}$ (atom/atom)
^{234}U	^{235}U	^{238}U	^{238}Pu	^{239}Pu	
393±21	12.4±1.7	317±17.4	N.D.	< 0.1	< 1.7×10^{-9}

N.D. — Not detected.

Sample size used for this analysis was 50g of the fine powder.

samples. In uranium minerals, the ^{239}Pu atom is known to be produced by neutrons from ^{238}U spontaneous fission, (α , n) reactions and cosmic ray neutrons of which the $^{239}\text{Pu}/^{238}\text{U}$ ratio is 10^{-12} (atom/atom). Also, the decay of superheavy nuclide present in nature should have produced measurable ^{239}Pu in the soil sample collected in 1933 when artificial plutonium was not known to be present in our environment.

If one does not assume that the Oklo phenomenon is still occurring inside the earth's crust today, it appears then that the observed plutonium anomaly in nature is a result of the input of man-made plutonium into the earth's environment and by volcanic eruptions.

The data presented in this report, however, indicate that the high $^{239}\text{Pu}/^{238}\text{U}$ ratios observed in the contemporary terrestrial samples are due to fallout contaminations.

Acknowledgement—This investigation was supported by the National Science Foundation under Grant ATM-8206718.

REFERENCES

- BISHOP, C. T., GLOSBY, A. A., BROWN, R. and PHILLIPS, C. A. (1978) Anion exchange method for the determination of plutonium in water: Single-laboratory evaluation and interlaboratory collaborative study, *NTIS PB-285*, 435, 55–56.
- CHERDYNTSEV, V. V., ZVEREV, V. L., KUPTSOV, V. M. and KISLITSYNA, G. I. (1968) Plutonium-239 in nature. *Geokhimiya* 1968, 395–401.
- DAVIS, W. D. and MEWHERTER, J. L. (1962) Abundance of U-236 in nature. *Geochim. Cosmochim. Acta* 26, 681–684.
- ESSIEN, I. O. (1983) Uranium, plutonium and thorium isotopes in the atmosphere and the lithosphere. Ph.D. Dissertation, University of Arkansas, Fayetteville, Arkansas.
- FIELDS, P. R., FRIEDMAN, A. M., MILSTED, J., LERNER, J., STEVENS, C. M., METTA, D. and SABINE, W. K. (1966) Decay properties of Pu-244 and comments on its existence in nature. *Nature* 212, 131–134.
- HAGEMANN, R., DEVILLERS, C., LUCAS, M., LECOMTE, T. and RUFFENACH, J. C. (1975) The Oklo Phenomenon. *IAEA, Vienna*, 415p.
- HARDY, E. P., KREY, P. W. and VOLCHOK, H. L. (1973) Global inventory and distribution of fallout plutonium. *Nature* 241, 444–445.
- HIROSE, K. and SUGIMURA, Y. (1981) Plutonium content of river water in Japan. *Pap. Met. Geophys.* 32, 301–306.
- HIROSE, K. and SUGIMURA, Y. (1983) Plutonium in the surface air in Japan, *Health Physics* (in press).
- HOFFMAN, D. C., LAWRENCE, F. O., MEWHERTER, J. L. and ROURKE, F. M. (1971) Detection of Pu-244 in nature. *Nature* 234, 132–134.
- KATSURAGI, Y., HIROSE, K. and SUGIMURA, Y. (1982) A study of plutonium fallout in Japan. *Rap. Met. Geophys.* 33, 85–93.
- KURODA, P. K. (1960) Nuclear fission in the early history of the earth, *Nature* 187, 36–38.
- KURODA, P. K. (1961) The time interval between nucleosynthesis and formation of the earth. *Geochim. Cosmochim. Acta* 24, 40–47.
- KURODA, P. K. (1982) *The origin of the chemical elements and the Oklo Phenomenon*. Springer-Verlag, Berlin-Heidelberg-New York.
- KURODA, P. K., ESSIEN, I. O. and SANDOVAL, D. N. (1983) Natural uranium from the eruption of Mount St. Helens. *J. Radioanal. Chem.* (in press).
- LEVINE, C. A. and SEABORG, G. T. (1951) The occurrence of plutonium in nature. *J. Am. Chem. Soc.* 73, 3278–3283.
- MEIER, H., BÖSCHE, D., ZEITLER, G., ALBRECHT, W., HEEKER, W., MENGE, P., UNGER, E. and ZIMMERHACKL, E. (1974) Anomalien der natürlichen Häufigkeit von ^{239}Pu . *Radiochim. Acta* 21, 110–116.
- MIYAKE, Y., KATSURAGI, Y. and SUGIMURA, Y. (1968) Deposition of plutonium in Tokyo through the end of 1966. *Pap. Met. Geophys.* 19, 267–276.
- MIYAKE, Y., KATSURAGI, Y. and SUGIMURA, Y. (1970) A study on plutonium fallout. *J. Geophys. Res.* 75, 2329–2330.
- MIYAKE, Y., SUGIMURA, Y. and SARUHASHI, K. (1973) Content of plutonium in river water in Japan. *Pap. Met. Geophys.* 24, 75–78.
- MIYAKE, Y., KATSURAGI, Y. and SUGIMURA, Y. (1975) Plutonium Fallout in Tokyo, *Pap. Met. Geophys.* 26, 1–8.
- PODOSEK, F. A. (1970) The abundance of ^{244}Pu in the early solar system. *Earth Planet. Sci. Lett.* 8, 183–187.
- PODOSEK, F. A. and LEWIS, R. S. (1972) ^{129}I and ^{244}Pu abundances in white inclusions of the Allende meteorites. *Earth Planet. Sci. Lett.* 15, 101–109.
- PRASOLOV, R. S. (1974) Geochemical isotope anomalies and the hypothesis of natural nuclear reactors. *Atomic Energy* 36, 57–59.
- ROWE, M. W. and KURODA, P. K. (1965) Fissiogenic xenon from the Pasamonte meteorite. *J. Geophys.*

- Res.* **70**, 709–714.
- SAKANOUE, M. and TSUJI, T. (1971) Plutonium content of soil at Nagasaki. *Nature* **234**, 92–93.
- SAKANOUE, M. and KOMURA, K. (1971) Anomalous high $^{234}\text{U}/^{238}\text{U}$ ratio in a neutral sample. *Nature Phys. Science* **233**, 80–81.
- SAKURAGI, Y., MEASON, J. L. and KURODA, P. K. (1983) Uranium and plutonium isotopes in the atmosphere. *J. Geophys. Res.* **88**, 3718–3724.
- SEABORG, G. T. and PERLMAN, M. L. (1948) Search for element 94 and 93 in nature: Presence of 94^{239} in pitchblende. *J. Am. Chem. Soc.* **70**, 1571–1573.
- TALVITIE, N. A. (1972) Electrodeposition of actinides for alpha spectrometric determination. *Anal. Chem.* **44**, 280–283.