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Geochemical Fractionation of Induced Radionuclides in Fresh Nuclear Debris through the Atmosphere—Np-239 and Co-60

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The atmospheric fractionation of induced radionuclides is discussed in some detail on the basis of results obtained by making a radiochemical analysis of fresh nuclear debris originating from recent Chinese nuclear test explosions. Among fresh nuclear debris particles collected at Niigata about 4000 km downwind from the Chinese test site, the trend for the enrichment of ^{239}Np was somewhat modified as compared with that derived from an averaged sample collected by a large-scale and high-altitude sampling procedure; more ^{239}Np was present in smaller-size fallout particles. Furthermore, it was found, in rain-water samples collected after the third Chinese nuclear explosion, that the atomic ratio at time-zero of ^{60}Co/^{95}Zr increased with a decrease in the ^{95}Zr-concentration in rain and *vice versa*. This suggests that the atmospheric fractionation of ^{60}Co-rich particles from ^{95}Zr-rich ones takes place during the travel of atomic clouds around the world.

Several papers[1–3] have been published on the atmospheric fractionation of nuclear debris of known origin. We have made a preliminary discussion of the unique fractionation behavior of ^{239}Np in fresh nuclear debris particles of a larger size which originated from the May 9, 1966, Chinese nuclear test explosion.[4] In this paper we will discuss in more detail the geochemical fractionation behavior of ^{239}Np. Furthermore, by comparing the fallout pattern of an induced nuclide ^{60}Co with that of a refractory fission product ^{95}Zr, we have established the geochemical fractionation of another induced nuclide, ^{60}Co; measurements of the variation in the ^{60}Co/^{95}Zr ratio, in fact, yielded experimental evidence for the geochemical fractionation of nuclear debris during the global circulation of the atomic clouds.

Experimental

Particle samples were collected on the roof of the 8-story Niigata City Hall; the roof surface was carefully surveyed by a G-M counter, and radioactive particles were picked off the roof, possibly along with a small amount of inactive dust material, and isolated under a microscope. Rain samples were collected by a stainless-steel funnel (1 m^2 in area) installed on the campus of the Niigata University. The radiochemical separation of each radionuclide was carried out by a combination of conventional precipitation, ion-exchange, and liquid-liquid extraction methods. The measurements of the radioactivity were made using a gas-flow counter or a NaI(Tl) scintillation detector (1¾ in$\times$1 in or 3 in$\times$3 in) with a 200-channel pulse-height analyzer.

Results and Discussion

Physical Properties of Hot Particles from the May 9, 1966 Explosion. A large number of highly-radioactive nuclear debris particles were detected within 36 hr of the third Chinese nuclear test on May 9, 1966. The individual particles, collected on May 11, ranged in total β-activity over a factor of 100, while the particles ranged in size from 5 to 24 μ in diameter. Particularly, sixteen single particles were carefully examined under a microscope; they were reddish-brown, and the particle ranged in size from 8 to 24 μ in diameter. The ^{95}Zr-content varied from 10^7 to 10^9 atoms/particle (Fig. 1), and the specific activity, from 2.3 to 7.3×10^{17} ^{95}Zr-equivalent fissions per gram. The average specific activities of surface-burst debris has been reported to be of the order of 10^{14} ^{95}Zr-equivalent fissions per gram, and air-burst debris particles are believed to have specific activities from 10^4 to 10^7 times higher.[5] Thus, the specific activity of the 16 single particles was

1) P. K. Kuroda, K. K. Menon and B. D. Palmer, "La pollution Radioactive Des Milieux Gazeux," Vol. 1, Saclay, France (1965), p. 105.

2) P. K. Kuroda, Y. Miyake and J. Nemoto, *Science*, **150**, 1289 (1965).

3) M. Thein and P. K. Kuroda, *J. Geophys. Res.*, **72**, 1673 (1967).

4) T. Sotobayashi, T. Suzuki and S. Koyama, This Bulletin, **40**, 1555 (1967).

5) E. C. Freiling and M. A. Kay, *Nature*, **209**, 236 (1966).

confined within a narrow range, the highest one among the reported specific activities observed in the case of a land-surface burst.

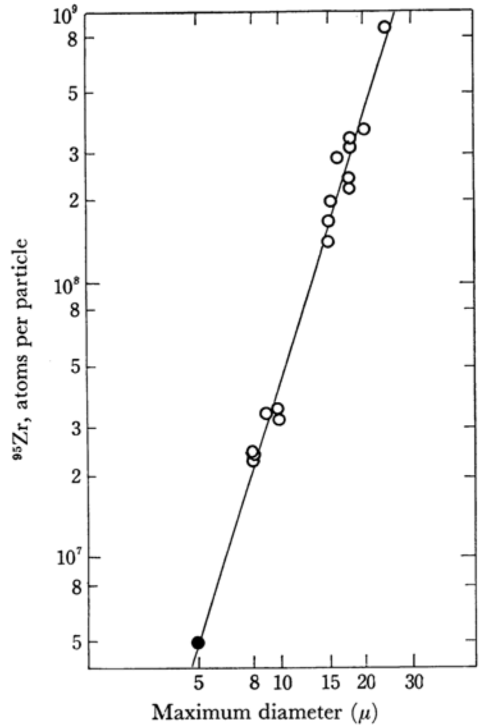


Fig. 1. Correlation between the number of ^{95}Zr atoms and the maximum diameter for 16 single particles collected on May 11, 1966.
●, the average number of atoms/particle for a combined sample of 9 particles.

Figure 1 shows the correlation between the particle size and the number of ^{95}Zr atoms for the 16 single particles. The number of ^{95}Zr atoms is plotted on a logarithmic scale as a function of the logarithm of the maximum diameter of an individual particle. In this graph the data points seem to lie near a solid line with a slope of 3.2. This finding implies that the atoms of ^{95}Zr are incorporated into a single particle with a uniform density. Moreover, the number of ^{95}Zr atoms could, in this case, be used for making a rough estimate of the particle size of nuclear debris.

Unique Fractionation Behavior of ^{239}Np. The debris particles of a larger size were strongly fractionated; concerning short-lived fission products (half-life, 1—3 days), the collected particles, about 250 particles, were all rich in refractory fission products, ^{97}Zr, ^{99}Mo and ^{143}Ce, and poor in ^{132}Te-^{132}I and ^{133}I, as would be expected from their chemical and nuclear properties in such larger particles. Most of the particles were poor in ^{239}Np, but some of them (less than 10 percent) were markedly rich in ^{239}Np, with no detectable amount of the ^{132}Te-^{132}I and ^{133}I in them, while a rain sample collected on May 10—11 was rich in volatile fission products, as is shown in Fig. 4. Figure 2 shows two γ-ray spectra of such two extreme-type particles, A and B; the total β-activity of the A particle was 1.1×10^5 pCi, and that of the B particle, 3.6×10^5 pCi, on May 11. Here the two spectra are normalized to equal the activity level of radiozirconium. The γ-ray spectrum obtained by plotting the difference in counts per channel between the two spectra had a shape similar to the γ-ray spectrum of ^{239}Np, as is shown in the inset. Figure 2 seems to suggest quite similar fractionation behavior in ^{97}Zr, ^{99}Mo, and ^{143}Ce in spite of the difference in ^{239}Np content.

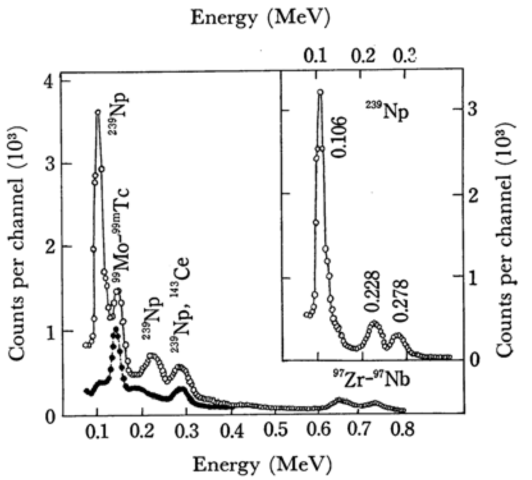


Fig. 2. Gamma-ray spectra of two extremely fractionated hot particles collected on May 11, 1966.
—○—, Particle A; —●—, Particle B

First, this result may be explained by the tentative assumption that the ^{239}Np found in A-type particles is not incorporated into debris particles simultaneously with such refractory fission products as ^{97}Zr at the earlier stages of the debris formation processes, but precipitates a little later on the surface of particles which had condensed at the earlier stages.[6] Further, according to the extensive studies by Freiling[5] and Crocker[7] on the radionuclide fractionation in nuclear debris particles, ^{239}Np originating from a land-surface shot seems to behave like a refractory group. The May 9, 1966, Chinese nuclear explosion was believed to have been blasted near the land surface; this belief is based on the fractionation data for the fallout particles collected in the lower stratosphere.[8] On the other hand, in the present observations, ^{239}Np

6) T. Mamuro, K. Yoshikawa, T. Matsunami and A. Fujita, *Health Physics*, **12**, 757 (1966).
7) G. R. Crocker, *Nature*, **210**, 1028 (1966).
8) H. W. Feely, C. Barrientos and D. Katzman, *ibid.*, **212**, 1303 (1966).

seemed to be present along with refractory fission products in less than 10 percent of the total particles collected. Here it should be mentioned that the particle samples studied in the present work were collected at ground level, at a particular location far away from the place of their formation and shortly after the explosion. Taking these points into consideration, such a unique distribution pattern of ^{239}Np and the observed narrow range of specific activity in the present samples may result mainly from the particular sampling conditions. From an alternative point of view, the present data may suggest the gravitational and meteorological forces and the differences in size and density among the debris particles combine to cause particle separation during the travel of the atomic cloud through the atmosphere. The fractionation behavior of ^{239}Np in this case seemed to be somewhat modified as compared with that seen in an averaged sample collected by a large-scale and high-altitude sampling procedure using air craft.

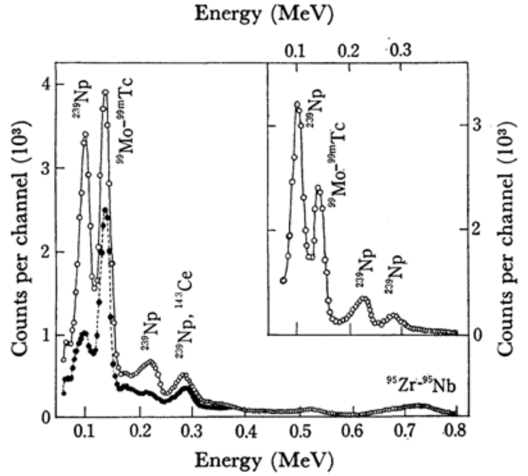


Fig. 3. Gamma-ray spectra of two composite particle samples, I and II.
—○—, Sample (I) of 9 paritcles;
—●—, Sample (II) of 8 particles.

Variation in the ^{239}Np Content with Particle Size. We have presented the γ-ray spectra of two composite samples in order to examine the change in the enrichment of ^{239}Np with the particle size; the particles were grouped in terms of their total β-activity. A combined sample (I) of 9 particles ranged in total β-activity from 10^3 to 10^4 pCi/particle 2 days after the explosion. Their average size was estimated to be 5μ in diameter by comparing their average atom number of ^{95}Zr per particle with a point on the experimental line (the solid circle in Fig. 1, 4.6×10^6 atoms/particle). The single particles of another composite sample (II) of 8 particles all had more than 10^5 pCi/particle when two days old; their average number of ^{95}Zr-atoms/particle was 2.1×10^8 atoms/particle, and their average diameter was estimated to be 16μ. Figure 3 shows the γ-ray spectra of the two combined samples measured 7 days after the explosion; these spectra are also normalized so as to be equal to the activity level of ^{95}Zr-^{95}Nb. These two composite samples were also poor in volatile fission products. The γ-ray spectrum shown in the inset of Fig. 3 was, as in Fig. 2, plotted by subtracting the γ-ray spectrum of the 9-particle sample from that of the 8-particle one. The spectrum in this inset indicates that the smaller-size particles were, on the average, richer in ^{239}Np than the larger ones. The 9-particle sample (I) belonged to the smallest-size range (5μ) among all the particles collected. Thus, the trend toward the enrichment of ^{239}Np may be believed to depend greatly upon the size of the debris particles.

It should be noted in Fig. 3 that smaller particles were also richer in nuclides with the photopeak at 0.14 MeV, mainly ^{99}Mo-^{99m}Tc, relative to ^{95}Zr-^{95}Nb. This, for reasons to be given below, may present a unique fractionation picture—that one of the most refractory nuclides, ^{99}Mo, shows the same enrichment trend as an induced nuclide, ^{239}Np; (1) the first member of the 99, mass chain, is the completely refractory 35.5-s ^{99}Zr (bp, 4750°C) and an earlier member of mass chain 95, with a significant half-life value, is a less refractory nuclide, 0.7-m ^{95}Sr (bp, 1366°C); (2) the time required for fission products to condense and to form a hot particle at earlier stages of particle formation processes is, on the average, 40 sec or less;[9] (3) larger particles are richer in more refractory fission products.[10] Taking these points into consideration, it may be expected that larger particles will be richer in ^{99}Mo than in ^{95}Zr. The present observations, however, exhibited quite the reverse tendency (Fig. 3).

It is tempting to make a somewhat speculative assumption on the origin of ^{99}Mo in order to explain this finding. Molybdenum metal is present as a minor constituent in the structural material of a nuclear-weapons device, and the isotopic abundance of ^{98}Mo for the element is 23.4%. Some fraction of the total ^{99}Mo observed might be produced by a ^{98}Mo(n,γ)^{99}Mo reaction which takes place during the nuclear fission. The ^{99}Mo fraction may then additionally precipitate on smaller-size particles in a way similar to that in which an induced nuclide, ^{239}Np, is deposited on smaller ones, as has been described above. This assumption is considered to be compatible with the fact that the fractionation correlation parameter of ^{99}Mo is dependent upon the total yield of a nuclear-weapons device.[5]

9) R. S. Clark, K. Yoshikawa, M. N. Rao, B. D. Palmer, M. Thein and P. K. Kuroda, *J. Geophys. Res.*, **72**, 1793 (1967).

10) S. H. Cassidy and R. G. Crocker, USNRDL-TR-67-70 (1967).

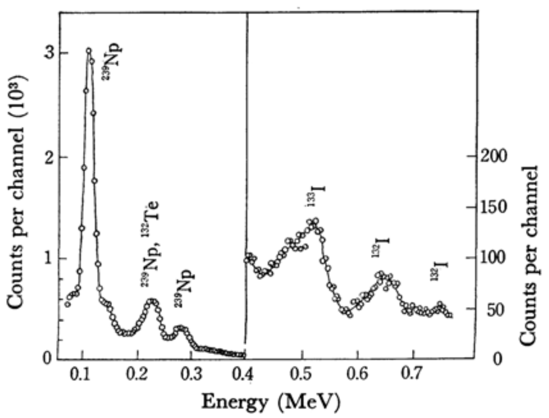
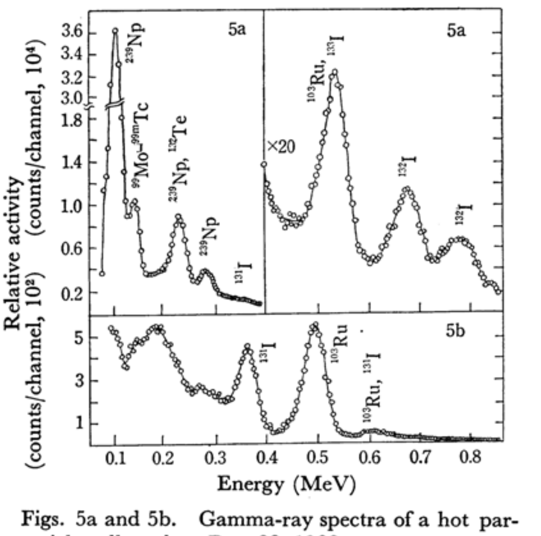


Fig. 4. The γ-ray spectrum of a rain sample (20 l) collected on May 10—11, 1966.

Np-239 in a Rain Sample. It is of interest to note that a rain sample (20 l) collected between 21 : 00 hr on the 10th and 5 : 00 hr on the 11th of May, 1966, before highly-radioactive particles were found in surface air at Niigata, had a unique radiochemical composition, consisting mainly of ^{239}Np, ^{132}Te-^{132}I and ^{133}I, with no detectable amount of refractory fission products, as is shown in Fig. 4. First, it is obvious in this figure that the ^{239}Np in the rain sample behaved nearly volatilely, while in the rain sample of May 15—16 the enrichment behavior of ^{239}Np was similar to that seen in the above-mentioned sample of 9 smaller-size particles. Secondly, this finding suggests that upper-air-borne particles rich in ^{239}Np, perhaps fine in size, first appeared in the atmosphere over Japan and that a part of them fell to the ground by means of wash-out in rain. Therefore, the observation of such rainwater activities also indicates that particle separation may have taken place to a considerable extent in the course of the 1.5-day travel of the atomic cloud from the Chinese test site to Japan.



Figs. 5a and 5b. Gamma-ray spectra of a hot particle collected on Dec. 28, 1966.
5a: A γ-ray spectrum measured 2 days after the explosion.
5b: A γ-ray spectrum measured 28 days after the explosion.

Np-239 in Hot Particles from the December 28, 1966, Explosion. More recently we have measured on December 30 the radioactivities of fresh nuclear debris; this debris evidently resulted from the fifth Chinese nuclear test explosion, on December 28, 1966. The highest total β-activity among all the single fallout particles collected was 4.9×10^4 pCi/particle 2 days after the explosion; most of the collected particles had a total β-activity of the order of $\sim 10^3$ pCi/particle an age of 2 days. Figures 5a and 5b show two γ-ray spectra for one such particle, measured 2 and 28 days after the explosion respectively. In Fig. 5a the two photopeaks at 0.67 and 0.78 MeV should be ascribed to ^{132}I, the daughter of ^{132}Te, and the contribution from ^{97}Zr-^{97}Nb radiations to the photopeaks is negligibly small. For this reason, the spectrum in Fig. 5b shows no discernible photopeaks arising from ^{95}Zr-^{95}Nb radiations with a half-life of 65 d in the 0.66—0.80 MeV range and only the well-defined photopeaks resulting from ^{103}Ru are recorded at 0.50 and 0.62 MeV. As a result, the measured particle consisted mainly of ^{239}Np and some volatile fission products, such as ^{131}I, ^{132}Te-^{132}I, ^{133}I, and ^{103}Ru. Thus, in this case, ^{239}Np behaved completely like the volatilely-behaving fission products observed in the rain sample collected on May 11, 1966 (Fig. 4).

Time Variation of the ^{60}Co/^{95}Zr Ratio in Rain Samples. Table 1 shows the experimental

TABLE 1. ATOM NUMBERS AT TIME-ZERO OF ^{95}Zr AND ^{60}Co AND THEIR RATIO IN RAIN SAMPLES

Period of collection 1966	Sample volume (l)	^{95}Zr (10^7 atoms)	^{60}Co (10^8 atoms)	^{60}Co/^{95}Zr
10—11 May	20	nd*		
15—16	24	1.9		
22—24	9	0.2		
28—29	32	31.4	15.3	4.9
5—6 June	18	12.5	16.3	13.0
9—11	18	4.8	23.8	49.7
20—22	23	8.7	4.7	5.4
24—27	15	4.7	1.4	3.0
28	48	16.9	0.8	0.5
2—3 July	32	4.8	2.2	4.6
7—9	36	2.5		
13	46	nd*		
15—18	174	6.4		
1—15 Aug.	16	3.6	0.2	0.6

* less than detection limits.

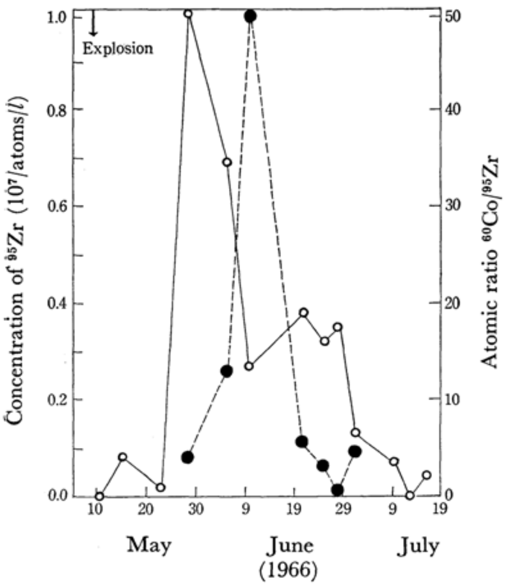


Fig. 6. Time variation of ^{95}Zr concentration and ^{60}Co/^{95}Zr in rainwater between May 11 and July 18, 1966.
—○—, ^{95}Zr concentration; ---●---, ^{60}Co/^{95}Zr

data on ^{60}Co and ^{95}Zr in rain samples collected between May 11 and August 15, 1966. Since no discernible photopeaks for these nuclides were found in the γ-ray spectra of rain samples collected before May 9, it was believed that the two nuclides originated only from the May 9, 1966, Chinese nuclear explosion. Figure 6 shows the ^{60}Co/^{95}Zr ratio at time-zero and the number of ^{95}Zr atoms/liter as a function of the time. First, it should be noted that no measurable amounts of ^{60}Co could be found in any particle or rain sample collected between May 11 and 24, shortly after the explosion. This still remains a puzzling question. It may, however, be seen from Fig. 6. that the ^{60}Co/^{95}Zr atomic ratio in rain increased with a decrease in the ^{95}Zr concentration, and *vice versa*. On the other hand, the first arrival at Niigata of the atomic clouds from the May 9, 1966, event brought about rainfalls with a very low concentration of ^{95}Zr (less than 10^6 atoms/l) on May 10—11, 16, and 24, but the two peak values of the ^{95}Zr concentration in the rain were found 19 and 40 days after the first arrival, as is shown in Fig. 6. The time taken for the atomic cluouds to circulate around the world has been estimated to be 3—4 weeks in spring and summer by measuring the time variation of some fission product ratios.[2)] As a result, these two peaks (Fig. 6) can possibly be ascribed to the second and perhaps even the third arrivals of the atomic clouds of the Chinese nuclear explosion, although the second peaks, around June 24, was not well defined. From these findings it is expected that the different distribution patterns between ^{95}Zr-rich and ^{60}Co-rich particles would be established in the rain-producing layers of the atmosphere during their fairly long travel of more than 20 days through the atmosphere. This suggests that the separation of ^{60}Co-rich particles from ^{95}Zr-rich particles would take place during their travel, and that the ^{60}Co-rich particles would remain a longer time than the particles rich in ^{95}Zr. This, therefore, provides evidence that ^{60}Co would be richer in smaller-size particles in the same way that ^{239}Np is.