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The dawn of radiochemistry in Japan

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Early history of radiochemistry in Japan / Kenjiro Kimura / Production of U-237 / Symmetric fission / Analysis of Bikini ashes

Summary. In the early history of radiochemistry in Japan Yoshio Nishina and Kenjiro Kimura were internationally known for their discovery of symmetric nuclear fission of uranium. They also succeeded in getting U-237, which is an $(n+1)$ series (neptunium series) nuclide, from U-238 by fast neutron irradiation. Kimura was an excellent leader of the radiochemical analysis of Bikini ashes in 1954. The results of that analysis contributed to the improvement of environmental radioactivity in the world. A tragic story of Nobuo Yamada working at the Radium Institute is related. The start of radiochemistry symposia in Japan is described.

1. Introduction

Masataka Ogawa (Fig. 1) was known for his presentation of the paper on nipponium [1] but it has not been well known that he was the first chemist among the Japanese who treated radioactivity. According to his report published in 1908 [2], "thorianite appears to contain still another new element, the oxide of which is radioactive". When he was studying nipponium at the University College London under the supervision of Sir William Ramsay (1904), Otto Hahn was also working at Ramsay's laboratory and found a new radioactive isotope radiothorium. Hahn's success should have been a strong impact on Ogawa. From the description of Ogawa's paper it is clear that he measured radioactivity of his samples. However, he could not continue any experiment on radioactive materials after coming back to Japan in 1906.

In 1909 Yohachiro Okamoto found a new radioactive mineral in Taiwan, and this was named Hokutolite by Kotora Jimbo at the University of Tokyo.

As a chemist Satoyasu Iimori at the Institue of Physical and Chemical Research was interested in radioactivity. He went to England to study radiochemistry under the direction of Frederick Soddy, the Nobel Prize laureate of 1921. After coming back to Japan in 1922, he surveyed Japanese minerals containing uranium and thorium. He improved a radon meter (known as IM Senkokei) in 1931, and this meter was used widely for the measurement of radon at hot springs in Japan and contributed to various studies on geochemical aspects related to radiochemistry.

Fig. 1. Masataka Ogawa (1865–1930).

2. Yamada at the Radium Institute

It is worthwhile to describe here the tragic life of Nobuo Yamada (Fig. 2) who worked with Marie Curie and her daughter Irène Curie. He graduated from Tohoku University in Sendai in 1919, and moved to the University of Tokyo in 1921, and then went to the Radium Institute in Paris in October 1923. He started working on the determination of the ranges of α-particles with Irène. His cautious and prudent manner in performing experiments and his diligence won

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Fig. 2. Nobuo Yamada (1896–1927) at work at the Radium Institute in Paris.

Fig. 3. Kenjiro Kimura (1896–1988).

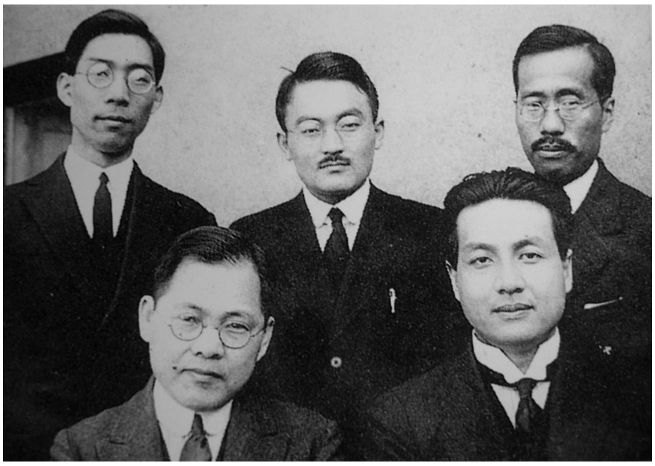

Fig. 4. Japanese students in Copenhagen; Nishina, front left and Kimura, front right.

her trust. He noticed disturbance by trace hydrogen (originating from water) in the determination of the range, and he constructed a new powerful equipment (Fig. 2) to observe the range exactly. An intense α-particle source was set in this equipment and water was thoroughly expelled. Thus he obtained reliable results concerning the α-particle range. Astonishingly he published 7 papers during his short stay in France. Irène wrote a letter to Marie Curie in which she described the usefulness of Yamada's new equipment [3]. Poirier, a French science historian, highly evaluated Yamada's work in his book "Marie Curie" [4]. He said that Yamada animated the atmosphere of the Institute. One chapter of that book was devoted to the work of Yamada.

After two years stay in Paris Yamada came back to Japan in February 1926. However, before starting any research work he suffered from a disease, most probably caused by radiation sickness, and died in 1927 at the age of 31. When a long time had elapsed after his tragic death, his scientific work was re-considered, and the cause of his disease was re-investigated in 1990s [5]. A strong contamination of his passport with radioactive material was clearly detected [6].

3. Radiochemical research with fast neutrons from a cyclotron

Yoshio Nishina at the Institute of Physical and Chemical Research in Tokyo constructed a cyclotron in 1937. This machine was not only used for research in physics but also in researches in several other fields. Radiochemical studies using fast neutrons generated by deuteron bombardment of lithium produced brilliant fruits. Cooperative work between different fields had been so far a rare case in Japan. Yoshio Nishina, a physicist and Kenjiro Kimura[1] (Fig. 3), a chemist at the University of Tokyo, had both studied in Copenhagen (Fig. 4) under the strong influence of Niels Bohr, working on the chemical effects of X-ray spectra. From 1938 onwards they started working together in Japan to elucidate some current topical problems in radioactivity research. In Italy Fermi's group had obtained some interesting results by irradiating many elements with slow neutrons. In particular, they irradiated uranium and observed β-emitting element(s) which they believed to be element 93. Fermi was awarded Nobel Prize in 1938. However, there arose some questions. French group Irène Curie and Pavel Savitch and German group Otto Hahn and Lise Meitner performed similar experiments, and they were perplexed because they observed much more complicated products.

Nishina and Kimura started their work by irradiation of thorium in early 1938. They found production of UY

[1] K. Kimura was a member of Editorial Advisory Board of this journal from 1962 to 1976. Editor

(Th-231) by $(n, 2n)$ reaction using fast neutrons [7]. This was an interesting example of conversion of a nuclide of the thorium series into a nuclide of the actinium series.

In the cooperative work Masao Ikawa assisted Kimura and played an important role in chemical analysis. He was an excellent analyst with highly polished technique and with sharp sense of judgment. He carefully used carrier materials to separate elements of ultramicro quantities. During the course of thorium irradiation experiments in 1938 he found silver radioactivity which resulted from thorium itself. Besides silver several elements could also be detected. Ikawa believed firmly the presence of silver. (This came from NUCLEAR FISSION of thorium, as was proved later.) At first, however, Kimura could not agree with his assistant's opinion and time was passing.

Otto Hahn and Fritz Straßmann in Berlin published a paper [8] concerning nuclear fission of uranium irradiated by slow neutrons, and Meitner and Otto Frisch in Cambridge interpreted this phenomenon correctly [9] in the beginning of 1939. The journals came to Japan in early 1939. Kimura instantly understood that silver formation in thorium irradiated by fast neutrons came from nuclear fission – different from Hahn's ASYMMETRIC fission. Then Nishina and Kimura and coworkers found some radioactive elements (Ag, Sn and Sb) produced by SYMMETRIC fission of thorium [10]. They continued their work on fission with fast neutrons in case of uranium and found many radioactive elements (Ru, Rh, Pd, Ag, Cd, In, Sn) [11–15]. G. T. Seaborg who was doing similar experiments highly evaluated this symmetric nuclear fission work [16].

Nishina and Kimura together with their coworkers did one more nice work by fast neutron irradiation of uranium in 1940. They observed the formation of U-237 which was recognized as a β-emitter [17]. This new nuclide belonged to $4n+1$ series (neptunium series). Meitner, Hahn and Straßmann had previously observed the formation of Th-233 which belongs to $4n+1$ series [18]. However, U-237 is meaningful for it is directly connected with Pu-237 which is usually considered to be the ancestor of neptunium series elements. In the case of U-237 its daughter should be the new element 93 which had been hitherto unknown. Nobufusa Saito, one of the students of Kimura, worked to detect this element, but was unsuccessful because of its very long half-life (about 2 million years). He wrote in his dissertation that the expected nuclide must have a very short or very long half-life. Meanwhile, in USA McMillan and Abelson [19] proved the formation of the element 93 from β-decay of U-239 produced by slow neutron capture of U-238. They adopted a recoil method to separate fission products from the element 93. Thus the element 93 was clearly identified and named neptunium. McMillan was awarded Nobel Prize together with Glenn T. Seaborg in 1951. It was recognized that neptunium is one of the $5f$ series elements. Saito remembered the loss of big success in discovering this new element. According to his comment Kimura expected that this element would behave like rhenium in the Periodic Table of the elements. It is regrettable that Japan was more or less isolated from the world scientific society at that time. The author infers that Nishina and Kimura probably regretted their own ignorance of the possibility of $5f$ series character of the element 93.

Because of wartime (Pacific War 1941–1945) restriction Nishina and Kimura could not continue these interesting studies using their cyclotron. When the war terminated by atomic bomb attack on Hiroshima and Nagasaki in August 1945, they lost many things for their experimental studies; and the occupation forces ordered to stop any studies related to atomic bombs and the nuclear science experiments. Unfortunately, the cyclotrons at the Institute of Physical and Chemical Research were broken and discarded by US soldiers.

Several years later, Nishina succeeded to import a radioisotope irradiated in a nuclear reactor from USA. Kimura and coworkers could resume chemical separation experiments using this irradiated unit.

4. Analysis of Bikini ashes

After the Second World War, USA and Soviet Union had been often colliding with each other over their political opinions. Therefore competition between USA and Soviet Union started in the development of nuclear weapons. USA began a test of hydrogen bomb which consisted of a liquid tritium and deuterium mixture using nuclear fusion on Eniwetok Island. Then a Russian scientist Sakhrov invented a hydrogen bomb consisting of LiD which was much more powerful than atomic bombs of Hiroshima-Nagasaki type using nuclear fission. USA also succeeded to make this type of bomb, and initiated its experiments on Bikini Atoll in the Pacific Ocean.

Unfortunately, a Japanese fishing boat the No. 5 Fukuryumaru was sailing in the vicinity of the Bikini Atoll on March 1, 1954. White ashes of the atoll fell down and covered the deck of the boat and 23 crew members of the boat suffered from radiation sickness because they were exposed to the strong radiation from radioactive materials included in the ashes. After coming back to Yaizu Port in Shizuoka they were sent to the hospitals in Tokyo (Hospital of the University of Tokyo and National Daiichi Hospital). One of them died later.

Kimura, at that time Dean of the Faculty of the University of Tokyo, was asked to analyze chemically the Bikini ashes to help physicians in medical treatment of the patients. He cooperated with Prof. Minami of the same university and all the members of both laboratories analyzed the radioactive materials in a relatively short time using various analytical methods [20].

Their results are briefly described here in Tables 1 and 2. The chemical composition of the ashes in Table 1 indicates that the ashes come from Bikini Atoll.

Kimura and Minami group used up-to-date techniques in their radiochemical analyses. Group separation of various radioactive nuclides was preformed by using carriers

Table 1. Chemical composition of ashes.

Composition	Percentage
CaO	55.2
MgO	7.0
CO_2	11.8
H_2O	26.0

Table 2. Summarized data of analysis.

Nuclide	Half-life	Percentage
Ca-45	152 d	0.2
Sr-89	53 d	1
Sr-90	19.9 y	0.02
Y-90	6.0 h	0.02
Y-91	61 d	8
Zr-95	65 d	5
Nb-95	35 d	3
Ba-140	12.80 d	5
La-140	40.0 h	6
Ce-141	33.1 d	7
Ce-144	282 d	2
Pr-143	13.7 d	16
Pr-144	17.5 min	2
Nd-147	11.3 d	9
U-237	6.75 d	20
Pu-239	24 360 y	*ca.* 4×10^{-4}

Other detected nuclides were: S-35, Nb-95m, Mo-99, Ru-103, Ru-106, Te-132, I-131, I-132, Nd-147, Pm-147.

according to ordinary analytical scheme and further by using ion-exchange resin. Then they identified individual nuclides by measuring with G-M counters. (Scintillation or semi-conductor detectors were not commercially available at that period in Japan). For plutonium and uranium, their α-particles were observed in a nuclear track plate and the track length of each nuclide was determined. They carefully calibrated counting efficiencies of G-M counters, and got absolute radioactivity of the ashes, and then estimated the specific radioactivity of 1.4 Curies/g (5.2×10^{10} Bq/g) on March 1, 1954. This was of course dangerous for the health of human beings.

The analytical results are summarized in Table 2.

As seen in Table 2, there are some nuclides which did not originate from nuclear fission. Ca-45 is a product of neutron capture of calcium as a constituent of the atoll. Presence of U-237 in a relatively large quantity was a surprise to Kimura because in his cooperative work with Nishina using a cyclotron he had discovered this nuclide as a result of $(n, 2n)$ reaction. When this analysis was published, military specialists argued that the nuclear bomb used in Bikini should be of a three-layered structure. As shown in Fig. 5, in the inner part of the bomb (consisting of plutonium) nuclear fission takes place. In the intermediate part which consists of LiD nuclear fusion is occurring as shown by successive reactions $^6Li(n, \alpha)^3H$ and $^3H(d, n)^4He$, and the outer layer is a tamper to suppress escape of inner materials. Nuclear fission is occurring here. Fast neutrons generated in the second layer attack outer uranium, resulting in U-237 by the $(n, 2n)$ reaction on U-238. This type of the bomb is called a 3F bomb because of the occurrence of fission-fusion-fission sequence in it.

Kimura presented the analytical results at the conference “Peaceful Uses of Atomic Energy” held in Geneva in 1955 [21]. Reinosuke Hara, a Japanese member of the International Atomic Energy Agency, attended the conference to hear Kimura’s lecture and wrote that there was a strong impact on the audience, and that this pioneering study played an important role to stop nuclear explosions in the atmosphere [22].

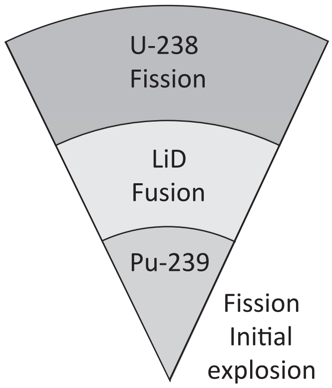

Fig. 5. 3F type hydrogen bomb.

5. Environmental radioactivity studies in Japan

The above study of Kimura and Minami clearly showed that global contamination by radioactive materials after nuclear detonation was very severe in the case of the 3F bomb using uranium fission. World-wide objection occurred against the nuclear explosion experiments. At last USA and Soviet Union (and United Kingdom) entered into the treaty stopping their experiments in the atmosphere (but not underground) in 1963. Fallout from the experiments clearly decreased since 1963.

A famous specialist of environmental radioactivity Eisenbud [23] dedicated his book “Environmental Radioactivity” to Kimura in 1979. He wrote his words as follows. “The Japanese edition of this work is dedicated to Kenjiro Kimura, whose pioneering work in the field of environmental radioactivity has contributed so much to world knowledge”.

In Japan the Bikini shock was so big that many university researchers got interested in the analysis of the ashes. Among them Takanobu Shiokawa at Shizuoka University (he moved to Tohoku University later) was noticed by a USA document writer in his book [24]. Kiba and Ohashi at Kanazawa University, Yamatera at Osaka City University, and Shimizu at Kyoto University took their parts in the analyses of the ashes.

It could be proper to say that Japanese environmental radioactivity studies began after this Bikini disaster. In many Japanese markets fishes from Pacific Ocean could not be sold and were discarded because of the radioactivity contamination of sea currents. Also radioactivity coming from fallout from the atmosphere stopped negotiation of tea in some Japanese markets. Thus Japanese scientists were strongly interested in environmental radioactivity research. Among them Miyake and Saruhashi at the Government Meteorological Bureau were noticed by the scientists in USA for their intensive works on environmental radioactivity. (Katsuko Saruhashi made her contribution to Japanese woman researchers by setting funds and prize later.) A Japanese ship Shunkotsumaru went for sailing to survey the radioactivity of sea water of west Pacific Ocean including Bikini Atoll. Scientists on board detected fission products in sea water samples. And they also detected Zn-65 (induced radioactivity from bomb material) besides fission products in fishes. Biological enrichment of Zn-65 was clearly shown in this case.

Fig. 6. Nobufusa Saito (1916–2007).

6. Start of radiochemistry symposia in Japan

Nobufusa Saito[2] (Fig. 6) at the University of Tokyo who was a student of Kimura started the first radiochemistry symposium in Tokyo in 1956.

The author remembers vividly that he presented interesting papers on hot atom chemistry of arsenic compounds adsorbed on a resin column. This symposium was the starting point of modern radiochemistry in Japan. In the same year the Japanese Government approved establishment of the Japan Atomic Energy Research Institute for the development and utilization of atomic energy for peaceful purposes. In this institute Kimura became one of the directors. The first nuclear reactor in Japan (JRR-1) started its operation in August 1957. Thus radiochemistry in Japan had overcome a hard period after the World War II and has been making progress until today. It should be noted that Saito contributed very much to this research field. He organized the 4th International Hot Atom Chemistry Symposium in Kyoto in 1966, and played an important role in setting the first Pacifichem (International Chemical Congress of Pacific Basin Societies) in Hawaii in 1979.

At last the author would like to note that the 50th anniversary of the radiochemistry symposium was celebrated in Mito City and Tokai Village in 2005 and the historical document was published in the form of a CD [25].

[2] N. Saito was a member of the Editorial Advisory Board of this journal from 1968 to 1996. Editor

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