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**DOI: 10.1016/j.crhy.2013.10.003**

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## Completion and extension of the periodic table of elements beyond uranium



### *Achèvement et extension du tableau périodique des éléments au-delà de l'uranium*

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## ARTICLE INFO

## Article history:

Available online 15 February 2019

## Keywords:

Radioactivity  
Radiochemistry  
Nuclear science  
Actinides  
Uranium  
Plutonium  
Periodic table of elements

## Mots-clés :

Radioactivité  
Radiochimie  
Chimie nucléaire  
Actinides  
Uranium  
Plutonium  
Tableau périodique des éléments

## ABSTRACT

In the 1940s, the search for elements beyond uranium led to the discoveries of the neutron-induced fission of uranium and of eleven trans-uranium radioelements, belonging to the actinide series. The best-known of the actinide elements is plutonium. Plutonium suffers neutron fission, as uranium, and, since 1940, humanity lives in the nuclear age, the age of the release of the fantastic nuclear energy. These discoveries resulted from continuous research efforts on natural radioelements, initiated in 1898 by Pierre and Marie Curie, and on artificial radionuclides, initiated in 1934 by Frédéric and Irène Joliot. Today, 118 elements are arranged into the modern versions of the periodic table. All the elements up to curium play a part in human activities. This paper describes how the progression of knowledge, thanks in particular to the heavy experimental means deployed in the USA before and during World War II, led to the completion and extension of the periodic table of elements. It focuses on the period 1937 to 1960 marked by the discoveries of manmade Tc (technetium), Pm (promethium), At (astatine), and of actinides from neptunium ( $Z = 93$ ) to lawrencium ( $Z = 103$ ). The discovery of Fr (francium) was the last discovery made in the line of the fruitful research on natural radioelements conducted in Europe.

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## R É S U M É

La recherche d'éléments au-delà de l'uranium dans les années 1940 a conduit aux découvertes de la fission de l'uranium par les neutrons, puis de onze éléments trans-uraniens classés dans la série des actinides, dont le représentant le plus connu est le plutonium. Le plutonium est fissile, comme l'uranium, et depuis cette époque l'humanité vit dans l'ère nucléaire, caractérisée par la libération de cette fantastique énergie. Ces découvertes s'inscrivent dans la suite des recherches conduites sur les radioéléments naturels, initiées en 1898 par Pierre et Marie Curie, et sur les radionucléides artificiels, commencées en 1934 par Frédéric et Irène Joliot. Aujourd'hui, 118 éléments sont regroupés dans le tableau périodique. Tous les éléments jusqu'au curium interviennent dans les activités humaines. Cet article montre comment la progression des connaissances a permis, grâce notamment aux moyens expérimentaux développés aux États-Unis juste avant et

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<https://doi.org/10.1016/j.crhy.2018.12.006>

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pendant la Deuxième Guerre mondiale, de compléter et d'étendre le tableau périodique, entre 1937 et 1960, par les découvertes du technétium (Tc), du prométhéum (Pm), de l'astate (At) et des actinides, du neptunium ( $Z = 93$ ) au lawrencium ( $Z = 103$ ), qui sont tous des radioéléments artificiels. La découverte du Fr (francium) a été la dernière découverte faite dans la lignée des recherches sur les radioéléments naturels conduites en Europe.

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## 1. Introduction

The periodic table of the chemical elements is essential to understand the properties of the matter in the universe. It is one of the most important achievements of mankind. It takes its modern form around the 1940s thanks to rapid progresses in nuclear science. This paper deals with these progresses, which, in less than one decade, led to its deep transformation by the discoveries of the trans-uranium elements included in the “actinide series”. The appendix gives an overview of the building of the knowledge in nuclear science, from 1899 to 1939, which prepared this transformation, at least from the point of view of a radiochemist. It is complementary to the two papers published in the *Comptes rendus Physique* that relate the discoveries of radioactivity [1] and of the neutron [2], as well as their impacts on nuclear science. Most of the selected references in this paper relate to review papers or books with authentic references to a discovery or to a given topic. Links to Wikipedia, if needed, are easy to find and are therefore not indicated.

## 2. Trends in nuclear science before the 1940s

Today, 150 years after the publication of Mendeleev's periodic chart, the periodic table includes elements from  $Z = 1$  up to  $Z = 118$  (Table 1). The United Nations have declared 2019 the International Year of the Periodic Table (IYPT) [3]. Between 1925 (discovery of last natural element rhenium Re,  $Z = 75$ ) and 1937, the periodic table was frozen. There were four vacant places in it, which was then not going beyond uranium, the heaviest element known at the time (Table 2). The missing elements were:  $Z = 43$  (technetium, Tc), 61 (promethium, Pm), 85 (astatine, At), and 87 (francium, Fr). Chemists had been unable to find natural elements to fill the vacant places despite the fact that chemistry was already a well-established science and industry, and that chemists were well aware of the periodicity of the properties of elements (lines) and of the similarity of the properties of homologous elements (columns) to guide their research. For instance, Tc was seen as an eka-manganese (eka-Mn) and so on, eka meaning “to be further discovered in a column of the periodic table”.

The completion of the periodic table and its extension beyond uranium came from research performed in the field of nuclear science. Indeed, all of the then still missing and trans-uranium elements are radioactive and manmade, except Fr, which exists in minute amounts on earth. The discovery of the first radionuclide ( $^{223}\text{Fr}$ ) belonging to the radioelement Fr has been completely in line with what could be expected from the decay of the known natural radionuclides, contrary to those of the radioelements Tc ( $^{95}\text{Tc}$ ), Pm ( $^{147}\text{Pm}$ ) and ( $^{211}\text{At}$ ), which were produced by nuclear reactions using cyclotrons.

In the early years of the 1930s, nuclear science comprised all of the topics driven by radioactivity, combining radiochemistry and physics, and the progresses in all the fields were progressing unceasingly. Nuclear science was based on a corpus of data gained from experiments on natural radioactivity since the discoveries made respectively by Henri Becquerel (1896), on the one hand, Gerald Schmidt (1898) and Marie Curie (1898), on the other hand, that uranium (U) and thorium (Th) emitted ionising rays (see appendix for details). Pierre and Marie Curie initiated the research on new radioactive elements with the discoveries of polonium (Po) and radium (Ra). The methodology that they used to isolate and concentrate the minute amounts of Po and Ra from uranium ores allowed the identification of many of the remaining natural radioactive elements and the preparation of radioactive sources for irradiation. Sources made using the radionuclide  $^{210}\text{Po}$  ( $T_{1/2} = 138$  d) were unique pure 5-MeV alpha emitters while those made using  $^{226}\text{Ra}$  ( $T_{1/2} = 1600$  y) or its daughter,  $^{222}\text{Rn}$  ( $T_{1/2} = 3.8$  d), emitted higher-energy alpha rays and beta and gamma rays.

The use of high radioactive sources of Po Ra and Rn led (1) through experiments performed to probe the matter at the atomic level, to clarify how to rank the isotopes of the elements into the periodic table according to the atomic numbers  $Z$  (number of protons) and  $N$  (number of neutrons), (2) through irradiation experiments performed to create new radionuclides to discoveries of artificial radioactivity (1934) [4] and fission of uranium (1938) [5]. The first of these discoveries extended the field of radiochemistry to that of nuclear chemistry. It was then possible to synthesise by nuclear reactions at least one radioactive isotope for all elements. In particular, it was recognised by Enrico Fermi that neutron irradiation of an element with atomic number  $Z$  could lead to a  $Z + 1$  radionuclide corresponding to the next element in the periodic table. The second discovery triggered the civilian and military nuclear age in which we are now living, which is the age of the release of nuclear energy,  $10^6$  times greater than electronic energy. The main contributors to these breakthroughs up to 1939 were teams of researchers from Europe.

Until the discovery of fission, the yields of nuclear reactions via irradiation with radioactive sources made from natural radionuclides were very low, even with the most intense Po and Ra sources that could be prepared by radiochemists. For

**Table 1**

Periodic table according to the IUPAC rules. Black, natural elements. Blue, natural radioelement. Red, artificial radioelements.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s		d										p					
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac** 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

** 5f	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 98	Fm 100	Md 101	No 102	Lr 103
* 4f	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

**Table 2**  
Periodic table around 1937. Boxes in red, missing elements. Black, natural elements. Blue, natural radioelements.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s		d										p					
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92												

* 4f	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
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instance, during a 15-min irradiation with a 100-mCi Po source ( $3.7 \cdot 10^9$  Bq) of a thin foil of monoisotopic aluminium ( $^{27}\text{Al}$ ), Frédéric and Irène Joliot produced no more than 250,000 radioactive atoms of phosphorus,  $^{30}\text{P}$  ( $T_{1/2} = 2.5$  min). The radioactivity was only about 1000 Bq. The yield was  $10^{-6}$  to  $10^{-7}$  atoms of  $^{30}\text{P}$  per alpha particle [4]. The Joliot's source was one of the higher  $^{210}\text{Po}$  source never prepared. Regarding the fission experiments by Otto Hahn and co-workers [5], it is estimated that an irradiation of 10 g of uranium with a flux of thermal neutrons of  $10^4$  n/cm<sup>2</sup>/s during half a day produced several  $10^6$  atoms of  $^{140}\text{Ba}$  ( $T_{1/2} = 12$  d), that is to say, 2 Bq! To increase the production by a factor 100, several days of irradiation were necessary. The activity of the source of neutrons, a mixture of radium salts and beryllium oxide, used in Hahn's fission experiments was 1.2 Ci of  $^{226}\text{Ra}$ ; it emitted around  $10^7$  n/s through the nuclear reaction  $^9\text{Be}(\alpha, n)^{12}\text{C}$ .

The other method to increase the production of radionuclides by irradiation has been to use beams of accelerated particles.

The first accelerators for light-charged particles (protons, deuterons, helium ions) were constructed in around 1930 and were soon after made available in the USA for irradiation of targets. The 37- and 60-inches Berkeley cyclotrons constructed by Ernest Lawrence and Stanley Livingston played a central role in the production of artificial radionuclides [6]. So, very quickly the alpha particle beams surpassed any Po or Ra source. An alpha particle beam of  $10^{-3}$  microampere is equivalent to 100 mCi of Po, and all particles are emitted in the same direction. The fluxes of neutrons produced by the nuclear reaction of deuteron with beryllium:  $^9\text{Be}(d, n)^{11}\text{C}$ , increased tremendously. Enrico Fermi constructed the first “nuclear reactor” in 1942 in Chicago, and high fluxes of neutrons were available rapidly.

As a consequence of these technological developments in the area of irradiation, nuclear science moved from Europe to the USA, where the still missing elements (except Fr) and the first trans-uranium elements were discovered just before the conflagration of World War II.

### 3. Discoveries of the missing elements of the 1937 periodic table

#### 3.1. Discovery of Fr

The existence of a radionuclide belonging to the Mendeleev's eka-caesium could be also predicted according to an alpha decay of  $^{227}\text{Ac}$ . Effectively, today it is well established that  $^{227}\text{Ac}$  decays to  $^{223}\text{Fr}$  ( $T_{1/2} = 22$  min) with an alpha branching ratio equal to 1.8%. This radionuclide has the longest half-life of all the francium isotopes. It has been discovered in 1939 [7a,8–11,12a].

The first attempts to detect and measure the alpha energy of  $^{227}\text{Ac}$  since 1914 were not conclusive, because of the presence of rare earths in the enriched  $^{227}\text{Ac}$  sources available at the time. Alpha particles were absorbed in the thickness of the source, and even electrons of low energy. So  $^{227}\text{Ac}$  was considered a soft beta emitter and was detected and measured by the gamma radiations of its daughters:  $^{227}\text{Th}$  ( $T_{1/2} = 18.7$  d) and  $^{223}\text{Ra}$  ( $T_{1/2} = 11.4$  d). In 1930, the available sources of  $^{227}\text{Ac}$  were still not carrier free. In 1935, Dan Hull, Willard Libby, and Wendell Latimer announced that the energy of electrons emitted by  $^{227}\text{Ac}$  was around 220 keV, an unexpected high value. That result triggered new researches at the “Institute du radium” in Paris, which led Marguerite Perey to discover and identify  $^{223}\text{Fr}$ .

She was working at this Institute under the guidance of Marie Curie and then of André Debierne. She was assigned the task of enriching  $^{227}\text{Ac}$  in co-precipitates of rare earths obtained from pitchblende, which had co-precipitated  $^{227}\text{Ac}$  in equilibrium with  $^{235}\text{U}$ , around five picograms per tonne of natural uranium. The only way to do that was to make fractional co-precipitations (see Appendix for rules of co-precipitation), a tedious, but necessary process to achieve carrier-free sources. She witnessed the accumulation of the short-lived daughters of  $^{227}\text{Ac}$ , which takes about three months to reach equilibrium. The high energy of beta rays obtained by Hull and co-workers seemed strange to Marguerite Perey. So, she decided to measure this energy again as well as to look at a possible new source of radioactivity, which could have been hidden by the growing of the daughters of  $^{227}\text{Ac}$ . She purified a  $^{227}\text{Ac}$ -rich co-precipitate of lanthanum oxide from the daughters of  $^{227}\text{Ac}$  and immediately measured the growing of the activity of a quasi-carrier-free source with a special ionisation chamber sensitive to low-energy electrons. During the first two hours, the activity increased more rapidly than expected from the growing of  $^{227}\text{Ac}$  daughters, with a half-life of about 20 min beginning at the end of the purification. She came to the conclusion that there existed a radionuclide hitherto unknown decaying by beta emission with an energy less than 80 keV. This low energy of the electrons was confirmed with the Wilson cloud chamber.

The new 20-min-half-life radionuclide was co-precipitated during the purification of Ac and seemed to arise from pure  $^{227}\text{Ac}$ , exempt of traces of its daughters, but its chemical nature should be more firmly established. She verified that it was not an isotope of thorium, radium, lead, bismuth, or thallium, to which daughters of Ac belong. Finally, she showed that it was co-precipitated with caesium perchlorate ( $\text{CsClO}_4$ ) and other salts of caesium. The activity of this co-precipitate decreased with a half-life of about 20 min. The unknown radionuclide belonged without doubt to the eka-caesium element with  $Z = 87$ . She named it francium, with reference to the choice of Marie Curie to name the first-discovered radioelement polonium. Francium was the last natural radioelement discovered

#### 3.2. Discovery of Tc

In 1937 [7b,12b], Carlo Perrier and Emilio Segré found that a “radioactivity” in a target of molybdenum (Mo) irradiated by deuterons (and neutrons) at the Berkeley cyclotron was co-precipitated with an organic complex of Re, but not with

molybdenum sulphide ( $\text{MoS}_3$ ) niobium oxide ( $\text{Nb}_2\text{O}_5$ ) or zirconium hydroxide ( $\text{Zr}(\text{OH})_4$ ). The co-precipitated radionuclide could not be heavier than rhenium (Re) but could belong to an eka-manganese. Indeed, according to the rules of nuclear reactions with deuterons (capture of the proton of the deuteron ion by the target), it was assigned the atomic number  $Z = 43$ , the main nuclear process being:  $^{94}\text{Mo}(\text{d},\text{n})^{95}\text{Tc}$ . In fact, stable Mo has seven isotopes, so other nuclear (d,n) reactions possibly occurred, leading to several radionuclides of technetium with a half-life allowing their detection. Indeed, the target, a part of the cyclotron deflector, has been sent by Ernest Lawrence (Berkeley) to Emilio Segré (Palermo). Its name was given by Segré to mark that it was the first manmade element. Tc is the eka-manganese predicted by Mendeleev. Later the radionuclide  $^{99}\text{Tc}$  was identified as a fission product.

### 3.3. Discovery of At

Many researchers have believed to have found eka-iodine ( $Z = 85$ ) as a natural element. In 1940, Dale Corson, Kenneth MacKenzie, and Emilio Segré produced  $^{211}\text{At}$  by irradiating a target of monoisotopic bismuth at the Berkeley cyclotron with alpha particles [7b,12c]. This radionuclide was produced according to the nuclear reaction  $^{209}\text{Bi}(\alpha, 2\text{n})^{211}\text{At}$ . Its half-life is 7.2 h. The chemical behaviour of this radionuclide was very close to that of iodine. Its biological behaviour was also similar to that of iodine, both concentrating in pig thyroids. The name astatine means instable. Indeed, the longest-lived isotope  $^{210}\text{At}$  has a half-life of 8.3 h. Three years later, several isotopes were found as short-lived daughters of small beta branchings of  $^{218}\text{Po}$  and  $^{215}\text{Po}$  belonging to  $^{238}\text{U}$  and  $^{235}\text{U}$  families.

### 3.4. Discovery of Pm

From the beginning of the 20<sup>th</sup> century until the 1940s, the entire research for element 61, as a member of the lanthanide series, had been unsuccessful. Jacob Marinski, Lawrence Glendenin, and Charles Coryell discovered the first isotope of the element of atomic number  $Z = 61$  around 1944 [7c,12b] when they were working in the Manhattan Project in Oak Ridge. They analysed carefully radionuclides produced all along the fission process of uranium and identified  $^{147}\text{Pm}$  ( $T_{1/2} = 2.2$  y) and  $^{149}\text{Pm}$  ( $T_{1/2} = 53$  h), but they announced their discoveries only in 1947. At that time, several trans-uranium elements had already been discovered.

## 4. Discovery of trans-uranium elements

The search for trans-uranium elements began when Enrico Fermi irradiated targets of uranium with neutrons soon after the discovery of artificial radioactivity [6,7c]. According to the periodical table at the time (Table 2), the first trans-uranium element should be an eka-rhenium, itself being a homologous element of manganese (Mn). He found that, in the acidic solution obtained by dissolution of the target in hydrochloric acid, a radionuclide exhibiting beta radioactivity and decaying with a half-life of 13 min was co-precipitated with manganese oxide ( $\text{MnO}_2$ ) and rhenium sulphide ( $\text{ReS}_2$ ). An additional beta emitter with a half-life of 23 min showed the properties of uranium. Fermi claimed the discovery of two trans-uranium elements. But this was criticised.

Several famous teams of radiochemists (Berlin, Paris) irradiated once again targets of uranium, purified from its daughters, with slow neutrons and came to an enigma. Fermi's new radioactivities were more or less confirmed. The Fermi's beta emitter of a half-life of 23 min was identified as  $^{239}\text{U}$ . But it was impossible, in the solution of dissolution of irradiated uranium, to identify by co-precipitations the new radioactivities, supposed to be emitted by radionuclides of homolog elements of Re, Os, Ir, and Pt ( $Z = 75$  to 78) or with radionuclides of Ra supposed to be daughters of some trans-uranium elements. The enigma was resolved when Otto Hahn [5] showed that these radioactivities were due to the radioactive fission products of uranium. As we know today, the irradiation of uranium gives rise to a mixture of fission products that are radionuclides belonging to many different elements, but the yields of production of radionuclides with  $Z = 75$  to 78 are insignificant. This is why the attempts to co-precipitate the emitters of these radioactivities with some compounds of Re, Os, Ir, Pt were unsuccessful.

In the historical experiments, which led to the discovery of fission of uranium by neutrons, the radioactivity measured with a Geiger Muller counter was low – about several hundred events/minute. The radioactivity of the daughters of  $^{238}\text{U}$  ( $^{234}\text{Th}$  and  $^{234\text{m}}\text{Pa}$ ), growing with a half-life of 24 d, was four to five times greater than that of the radioactivity induced by neutron irradiation, and the production of radionuclides of trans-uranium was 15 times less than that of fission products. Even with fresh purified uranium, measuring the radioactivities that were supposed to be due to trans-uranium radionuclides remained very difficult and nearly impossible in the presence of fission products.

However, by early 1940, Edwin McMillan and Philip Abelson irradiated a thin foil of uranium with neutrons and showed by careful measurements that a beta emitter with a half-life of 2.3 d did not escape the foil, while fission products did, due to their extremely high recoil energy. During the spring of 1940 in Berkeley, this observation became the breakthrough that led to the discovery of neptunium. Indeed, it was in agreement with the formation of a radionuclide, which, decaying by beta emission, could confer on its daughter a low recoil energy, like  $^{239}\text{U}$ , produced by the radiative neutron capture on  $^{238}\text{U}$ :  $^{238}\text{U}(\text{n},\gamma)^{239}\text{U}$ .



#### 4.1. Discovery of neptunium

Edwin McMillan and Philip Abelson irradiated a fine layer of a uranium compound ( $\text{U}_2\text{O}_7(\text{NH}_4)_2$ ) not containing any uranium daughters. They used the neutrons produced by the impact of a beam of deuterons on a Be target and not the traditional Ra/Be neutron source. The radioactivities produced, for example during one hour with a few hundred microamperes of deuterons, were higher than those available with the best Ra/Be sources, but remained around a few hundred Bq.

The following discussions address mainly the chemistry of trans-uranium elements, which is complicated because they display several oxidation states, 3 to 6, connected through redox chemical reactions. These oxidation states are indicated by roman digits, for instance U(VI) for hexavalent uranium (oxidation state 6), U(IV) for tetravalent uranium (oxidation state 4) and so on for the other oxidation states and the other elements. The physicochemical properties of an element are dependent of its oxidation state.

After dissolution of the uranium target in strong acidic solution (without fission products), they compared the chemical behaviour of the 2.3-d half-life radioactivity retained in the foil with those of Re and U. This radioactivity was not co-precipitated by hydrogen sulphide ( $\text{H}_2\text{S}$ ) as rhenium sulphide ( $\text{ReS}_2$  or  $\text{Re}_2\text{S}_7$ ), neither reduced in metal with Re by Zn, nor not-volatilized with Re in the form of oxide ( $\text{ReO}_4$ ). In the presence of potassium bromate ( $\text{BrO}_3\text{K}$ ) acting as oxidant (couple  $\text{BrO}_3^-/\text{HBrO}^-$ ), it was not co-precipitated by hydrofluoric acid (HF) as cerium fluoride ( $\text{CeF}_4/\text{CeF}_3$ ), but remained in solution with U. However, it was co-precipitated by acetic acid (acac) as mixed sodium uranium (UVI) acetate ( $\text{UO}_2(\text{acac})_2$ ). After processing of the oxidizing bromate solution by  $\text{SO}_2$ , (couple  $\text{SO}_2/\text{SO}_4^{2-}$ ), which makes the solution reducing, the radioactivity was co-precipitated by HF with  $\text{CeF}_3$  or with thorium iodate ( $\text{IO}_3)_4\text{Th}$  or thorium peroxide ( $\text{ThO}_4$ ). The behaviour of the radionuclide with a half-life of 2.3 d was close to that of uranium during an oxidoreduction cycle and different from that of rare earths, even if it was co-precipitated with the trivalent cerium present in the reducing solution ( $\text{CeF}_3$ ). McMillan and co-workers named neptunium (Np) the element of which the new radionuclide was an isotope. It has been identified as the daughter of  $^{239}\text{U}$ , synthesized according to the nuclear reaction  $^{238}\text{U}(\text{n},\gamma)^{239}\text{U}$ .

It is known today that Np(V) and U(VI) are the stable oxidation states of Np and U. In the conditions of the MacMillan experiment the bromate anions possibly oxidized Np(V) to Np(VI), which are not co-precipitated with  $\text{CeF}_3/\text{CeF}_4$  and  $\text{SO}_2$  reduced Np(V) to Np(IV)/Np(III), which are co-precipitated with  $\text{CeF}_3$ . In contrast,  $\text{SO}_2$  did not reduce U(VI) to U(IV). Likewise cerium, in the presence of the bromate anion, was possibly present as Ce(III) or Ce(IV).

The first chemical proof of the existence of a new family of elements, with a very complicated chemistry, dates back to the spring of 1940. It was obtained with no more than  $3 \cdot 10^7$  atoms of  $^{239}\text{Np}$ . McMillan thought that neptunium could belong to an “uranide series”. This new idea of a sensitivity of the trans-uranium elements to the redox potential of the respective solutions will lead to the discovery of the first isotope of the second trans-uranium element with  $Z = 94$ :  $^{238}\text{Pu}$ .

In addition to the chemical experiments that McMillan performed, he measured, by the fall of 1940, some characteristics of the beta decay of  $^{239}\text{Np}$  and of its daughter. Indeed, the beta decay of  $^{239}\text{Np}$  generates  $^{239}\text{Pu}$ , and he wanted to look at this. He concluded that this radionuclide should be a long-lived alpha radionuclide, if indeed it was really an alpha emitter. McMillan did not find any new radioactivity produced by the decay of a  $^{239}\text{Np}$  sample that he had prepared, despite the use of a proportional counter able to measure alpha activity. In fact, the quantity eventually produced was undetectable, as we know today, the half-life of  $^{239}\text{Pu}$  (24,000 y) being too long to give a detectable alpha radioactivity.

#### 4.2. Discovery of plutonium

The discoveries of the two first isotopes of the next element beyond Np:  $^{238}\text{Pu}$  and  $^{239}\text{Pu}$  occurred in 1941 at Berkeley, in the context of a demand of many European scientists asking the USA to take in hands the post-fission researches. An “Advisory Committee on Uranium” appointed by the President of the USA at the end of 1939 looked at the interest of uranium research. Such researches were already implemented in Berkeley around the cyclotrons. At the end 1941 after the discovery of plutonium the results were classified, up to 1946. By the fall of 1941, it appeared possible to set up atomic bombs with fissile uranium and plutonium and the highly secret “Manhattan project” started in December 1942. It received top priorities on enrolling the best scientific people and material. When it was found, in 1942, that kilograms of  $^{239}\text{Pu}$  could be possibly produced by massive irradiation of uranium, a special project, whose code name was “Metallurgical Laboratory”, sited at Chicago, was dedicated to research on plutonium. The steps from identification to production of plutonium from minute amounts to kilogram scale are reviewed in the following, according Glen Seaborg [6].

After the first findings of McMillan on the daughter of  $^{239}\text{Np}$ , it appeared necessary to increase the production of this radionuclide and to look also for an isotope of Pu more easily detectable than  $^{239}\text{Pu}$ . That seemed achievable for McMillan and Seaborg. Arthur Whal and Joseph Kennedy started preliminary tests, by the end of 1940. They irradiated 5.5 g of uranium oxide ( $\text{U}_3\text{O}_8$ ) in the Berkeley cyclotron by both neutrons and deuterons.

The produced fraction of Np was isolated from uranium oxide by using the known protocol: dissolution in acidic solution, oxidation by  $\text{BrO}_3\text{K}$  followed by reduction with  $\text{SO}_2$  and co-precipitation by a tetravalent carrier, for instance thorium tetrafluoride  $\text{ThF}_4$ . An alpha activity was perfectly detected in this precipitate at the same time as an increase of beta radioactivity with a half-life of around 2 days, close to that of pure  $^{239}\text{Np}$ , but different in energy. Seaborg’s team subsequently performed experiments to identify the new alpha radionuclide using a proportional counter able to measure alpha radiation without interference with beta radiation.



After dissolution of the thorium fluoride in an acidic solution and in the presence of bromate anions, the alpha radioactivity co-precipitated with thorium fluoride ( $\text{ThF}_4$ ), while the beta radioactivity, supposedly  $^{239}\text{Np}$ , did not co-precipitate as it was indeed already known from the previous experiments. Thus, the new radionuclide was not as easily oxidised as Np. But, in the presence of a very powerful oxidizer – potassium peroxy-disulfate coupled with silver as catalyst (couple  $\text{S}_2\text{O}_8^{2-}/\text{Ag}^{2+}/\text{HSO}_4^-/\text{Ag}$ ) – the alpha radioactivity did not precipitate. The alpha emitter radionuclide remained in solution with the beta emitters, as expected from the behaviour of  $^{239}\text{Np}$ .

By the spring of 1941, the radionuclide associated with the alpha activity showed a clearly different behaviour than that of the one exhibiting the beta activity. The Seaborg group concluded that it was an isotope of the element  $Z = 94$  produced by the decay of a new isotope of Np. Indeed, the irradiation of  $^{238}\text{U}$  had produced  $^{239}\text{Np}$  and  $^{238}\text{Np}$ , both beta emitters with close half-lives (2.3 d and 2.1 d), the latter decaying to  $^{238}\text{Pu}$ , an alpha emitter with a long half-life (estimated to 50 y) but shorter than that of the long-lived  $^{239}\text{Pu}$ . The nuclear reactions were:  $^{238}\text{U}(\text{d},\text{n})^{238}\text{Np}$  and  $^{238}\text{U}(\text{n},\gamma)^{239}\text{Np}$ .

The challenge of McMillan and Seaborg had been met in only several months. The publication on the discovery of  $^{238}\text{Pu}$  occurred in 1946, five years later. The element  $Z = 94$  was named plutonium in 1942.

We know today that the chemical behaviour of Pu and Np was consistent with the redox potentials of all the species present in the acidic solutions implemented in the historical experiments: peroxy-disulfate anions oxidize Np and Pu into  $\text{Np(VI)}$  and  $\text{Pu(VI)}$ , not co-precipitated by thorium tetrafluoride ( $\text{ThF}_4$ ), and that  $\text{SO}_2$  reduces them to  $\text{Np(IV)}$  and  $\text{Pu(IV)}$ , co-precipitated with  $\text{ThF}_4$ .

The discovery of  $^{238}\text{Pu}$  and  $^{239}\text{Pu}$  opened the possibilities to study the chemical properties of plutonium, starting at the scale of traces ( $^{238}\text{Pu}$ ) and ending up at quantities normally used for any more abundant element ( $^{239}\text{Pu}$ ), in particular those properties that differentiated it from Np and from the fission products.

The first step before starting experiments was to obtain solutions of  $\text{Np(IV)}$  and  $\text{Pu(IV)}$  from irradiated uranium and the second one was to separate Pu from Np. The protocol to achieve the first step was for instance (1) the dissolution of irradiated uranium in acidic solution, (2) the processing of the solution according the peroxydisulphate– $\text{Ag}/\text{SO}_2$  cycle that produced first  $\text{Pu(VI)}$  and  $\text{Np(VI)}$ , and then  $\text{Pu(IV)}$  and  $\text{Np(IV)}$ , with most of the fission products removed, (3) the co-precipitation of tetravalent Np and Pu from the solution. The protocol to separate Np/Pu was (1) to dissolve the co-precipitate in acidic solution, (2) to oxidise selectively  $\text{Np(IV)}$  to  $\text{Np(V)}$  by bromate anions, (3) to co-precipitate  $\text{Pu(IV)}$ .

Many experiments were performed according to these protocols, which showed that Pu had a behaviour close to that of U and Np, but a different of that of Os, as it was expected at the beginning of the search for trans-uranium elements.

To obtain  $^{239}\text{Pu}$  in microgram amounts, it was necessary to increase the production of  $^{239}\text{Np}$ . It is from 1.2 kg of uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2$ ) irradiated during two days with slow neutrons at the Berkeley cyclotron that, for the first time, 0.5  $\mu\text{g}$  of  $^{239}\text{Pu}$  was produced by decay of  $^{239}\text{Np}$ . The protocols of separation were adapted to the quantity of uranium irradiated by extracting the mass of uranium in a diethyl ether organic phase. By repeating six times the fractional co-precipitation of  $\text{Pu(IV)}$  with  $\text{ThF}_4$ , one obtained precipitates increasingly rich in  $^{239}\text{Pu}$ . It is with the final fraction containing 0.5  $\mu\text{g}$  of  $^{239}\text{Pu}$  that Seaborg showed that the fission of  $^{239}\text{Pu}$  had a yield 50 times better than that of  $^{235}\text{U}$ . Thus, in the spring of the year 1941, a new possibility to release massively nuclear energy was appearing, besides the use of highly  $^{235}\text{U}$ -enriched uranium. With respect to this topic, it is interesting to note that in early 1939 Frédéric Joliot gave the proof that the neutron induced fission of uranium emits three neutrons, making possible a nuclear chain reaction. The same was expected for plutonium.

The next step in the historical production of  $^{239}\text{Pu}$  was to get compounds of Pu “visible by the eyes”. Tens of kilograms of uranium ( $\text{U}_3\text{O}_8$ ) were irradiated by thermal neutrons in Berkeley and Saint Louis cyclotrons and then processed as said above. From the last precipitate, enriched in  $^{239}\text{Pu}$ , the first micrograms of pure compounds, fluoride ( $\text{PuF}_4$ ) and oxide ( $\text{PuO}_2$ ), could be prepared. The first visible plutonium oxide weighed 2.8  $\mu\text{g}$  obtained from a 10-mL solution of concentrated Pu. It was achieved in the fall of 1942. Only about 2 mg of  $^{239}\text{Pu}$  were produced using cyclotrons.

It was clear in 1942 that, for military purpose, the way to obtain kilogram quantities of  $^{239}\text{Pu}$  was the irradiation of tonnes of uranium in nuclear reactors where it is produced as other isotopes ( $^{238}\text{Pu}$  to  $^{243}\text{Pu}$ ) by successions of complicated nuclear processes. The isotopic composition of plutonium depends on time of irradiation, the lesser giving the higher  $^{239}\text{Pu}$  percentage. By the end of 1942, a complex for the production of plutonium was launched at Hanford. This was within the framework of the “Metallurgical Laboratory”. In 1944, three dedicated reactors and a reprocessing facility were in full operation. The reactors were fuelled with natural uranium (150 tonnes), moderated with graphite (1300 tonnes) and cooled with water. Around 100 g/d of military plutonium were produced ( $^{239}\text{Pu} > 93.7\%$ ). Three years after launching the project, enough  $^{239}\text{Pu}$  was available to make two atomic bombs. The first industrial processes of separation of large quantities of Pu from irradiated uranium was based on the use of redox cycles and co-precipitations of Pu as bismuth phosphate ( $\text{BiPO}_4$ ), and finally on the precipitation of plutonium phosphate itself ( $\text{Pu}_3(\text{PO}_4)_4$ ). Later, in 1956, the Purex process replaced the phosphate process.

Today, an improved Purex process is used to reprocess the nuclear spent fuel from electronuclear reactors. Basically, in the Purex process,  $\text{U(VI)}$  and  $\text{Pu(IV)}$  are co-extracted in an organic phase from an acidic aqueous solution where the spent fuel is dissolved.  $\text{Pu(III)}$  is in turn extracted from the organic phase using a reducing aqueous solution. Fission products remain in the original acidic aqueous solution. The advantages of solvent extraction over co-precipitation to process radioactive matter are numerous. However, let us recall that fractional co-precipitation has supported the radium industry from 1900 to 1940. The world production of radium at the time has been only one kilogram. Today, each tonne of spent fuel unloaded from electronuclear reactors contains around 10 kg of plutonium and 370,000 metric tonnes have been already unloaded, of which 30% have been reprocessed by the Purex process [15].

#### 4.3. Discoveries of Am and Cm

Seaborg thought, as MacMillan did before, that the next elements beyond Pu with  $Z = 95$  and  $96$  should have more or less the same properties as Np and Pu, belonging to a “uranide series”. In line with the previous experiments, they irradiated targets of  $^{239}\text{Pu}$  with deuterons and neutrons at the Berkeley cyclotron and they looked at oxidizing the radionuclides bearing new alpha radioactivity to bring them to their highest oxidation state, a method that has been key in discovering the two first trans-uranium elements. But they failed in identifying them. In 1944, Seaborg changed his thinking in favour of the idea that the trans-uranium elements could possibly belong to a “heavy rare-earth series”, starting with actinium. If that hypothesis was right, elements  $95$  and  $96$  should be homologous elements to europium (Eu) and gadolinium (Gd), easy to identify by co-precipitation with lanthanum compounds as trivalent elements. Effectively, the irradiation of  $^{239}\text{Pu}$  by helium ions at the Berkeley cyclotron generated an alpha radioactivity that could be co-precipitated with lanthanum fluoride ( $\text{LaF}_3$ ) and that was identified as the decay of  $^{242}\text{Cm}$  ( $T_{1/2} = 162$  d). The radionuclide was produced according to the nuclear reaction:  $^{239}\text{Pu}(\text{He}, 2n)^{242}\text{Cm}$ . The experiments were performed by a team comprising Glenn Seaborg, Ralph James and Albert Ghiorso. Later they showed that the well-known  $^{238}\text{Pu}$  was the daughter of  $^{242}\text{Cm}$ . The same year Seaborg published a new periodic table including an “actinide series”.

One year later (1945), Glenn Seaborg, Leon Morgan, and Albert Ghiorso chemically identified the first radionuclide with  $Z = 95$ :  $^{241}\text{Am}$ . It was produced from a target of  $^{239}\text{Pu}$ , irradiated by neutrons in a nuclear reactor at the Metallurgical Laboratory, where Fermi’s Chicago Pile-1 reactor had been rebuilt.  $^{241}\text{Am}$  ( $T_{1/2} = 430$  y) is the daughter of  $^{241}\text{Pu}$  ( $T_{1/2} = 14$  y) produced by successive neutron radiative captures by  $^{239}\text{Pu}$ . The trivalent state of Am identified by co-precipitation with  $\text{LaF}_3$  was confirmed by volatilisation of  $^{241}\text{Am}$  from the deposit of mass  $241$  obtained with a mass spectrometer. The deposit contained both  $^{241}\text{Am}$  and  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$  being the most volatile. By radiative neutron capture,  $^{241}\text{Am}$  can be converted into  $^{242}\text{Am}$  ( $T_{1/2} = 16$  h), which decays by beta emission to  $^{242}\text{Cm}$ .

It is noteworthy that the Berkeley teams identified filiations between the new trans-uranium radionuclides that were consecutively discovered, which was critical key to the identification of the next ones.

#### 4.4. Discoveries of the trans-curium elements

The discoveries of the following trans-uranium elements (actinides) lasted from 1949 to 1960. They were all produced by nuclear reactions. The idea was to irradiate targets of some isotopes of the actinide element already discovered with particles to get new radionuclides with atomic numbers higher than that of the target and to identify them as trivalent elements. To do that, it was necessary (1) to have sufficient quantities of the right radionuclides to prepare the targets, (2) to dispose of intense beams of high-energy particles to irradiate the targets, (3) to be equipped with new sensitive detectors for radioactivity measurement, (4) to have faster and new chemical processes than the historical co-precipitation ones to separate and to identify new radionuclides from complex mixtures of radionuclides, and (5) to benefit from the development of fast nuclear techniques to catch the few radioactive atoms produced in nuclear reactions with heavy ions and to do chemistry at “one atom at a time”. Indeed, as  $Z$  increases, the yields of production of new radionuclides decrease drastically.

All these requirements were met progressively during the ten years from 1949 onwards at the cost of tremendous efforts. For instance, Am and Cm were respectively produced in milligram and microgram amounts by irradiation of Pu and Am by an intense flux of neutrons in a high-flux nuclear reactor at Oak Ridge. In 1949 they were used as targets to produce  $^{243}\text{Bk}$  ( $Z = 97$ ,  $T_{1/2} = 4.5$  h) and  $^{245}\text{Cf}$  ( $Z = 98$ ,  $T_{1/2} = 44$  min) by nuclear reactions with helium ions. The next radionuclides discovered belonged to the elements beyond Cf:  $^{253}\text{Es}$  and  $^{255}\text{Fm}$ . They were found in the debris of the Mike thermonuclear explosion in 1952. Three years later, the first isotope of elements with  $Z = 101$ , Md, was produced by:  $^{253}\text{Es}(\text{He}, n)^{256}\text{Md}$  (EC,  $T_{1/2} = 1$  d). The radionuclides of the last two actinides were synthesized in 1958 and 1961, with highly charged particles available in Berkeley, but also at the same time in Stockholm and Dubna, according to:  $^{246}\text{Cm}(^{12}\text{C}, 4n)^{254}\text{No}$  and  $^{249-252}\text{Cf}(^{10-11}\text{B}, xn)^{258}\text{Lr}$ .

The historical nuclear reactions that enabled the discoveries of the radionuclides of the trans-curium elements had been prepared by numerous experiments of irradiation and of chemical identification. Indeed, the nuclear reactions generated intricate mixtures of radionuclides. Table 3 gives an overview of the discoveries of trans-curium radionuclides.

An important step toward the identification of Bk to Fm at the tracer scale down to a few atoms, in addition to conventional co-precipitation, had been made according to their rank of elution from a Dowex cation exchanger by a solution of ammonium alpha-hydroxy-isobutyrate, the heaviest elements coming first: Fm to Bk [14].

During the 10 years from 1949 to 1960, the number of researchers more or less involved in the experiments to produce heavy actinides increased considerably. This period corresponds also to the rise of military nuclear energy with massive production of  $^{239}\text{Pu}$  in dedicated nuclear reactors and, consequently, of large quantities of actinide elements up to Cm. Today the quantities of these elements accumulated in the spent fuel from worldwide electronuclear reactors are considerable [15]. Their isotopic compositions are variable, depending on the burn-up of the fuel. For instance, civil plutonium is a mixture of isotopes ranging from  $^{238}\text{Pu}$  to  $^{242}\text{Pu}$  [7d,16].

**Table 3**

Discovery, production, and identification of trans-curium elements.

a	1949	$^{241}\text{Am}(\text{He}, 2\text{n})^{243}\text{Bk}$ ( $\alpha$ , 4.5 h) $^{241}\text{Am}(\text{He}, \text{n})^{244}\text{Bk}$ (CE, 4.35 h)* $E_{\text{He}} = 35 \text{ MeV}$ , $10 \mu\text{A}/\text{cm}^2$ , Berkeley	7 mg of $^{241}\text{Am}$ , several thousand atoms of Bk
b	1950	$^{242}\text{Cm}(\text{He}, \text{n})^{243}\text{Cf}$ ( $\alpha$ , 44 min) $E_{\text{He}} = 35 \text{ MeV}$ , $10 \mu\text{A}/\text{cm}^2$ , Berkeley	$\mu\text{g}$ of $^{242}\text{Cm}$ , 5 000 atoms of Cf
c	1952 1955	$^{238}\text{U}$ ( $15\text{n}$ , $7\text{e}^-$ ) $^{253}\text{Es}$ ( $\alpha$ , 20 d) $^{238}\text{U}$ ( $18\text{n}$ , $8\text{e}^-$ ) $^{255}\text{Fm}$ ( $\alpha$ , 22 h) Argonne National Laboratory, Chicago, Los Alamos Scientific Laboratory, Albuquerque	kg of $^{238}\text{U}$ , hundreds of atoms of Es and Fm. Mike explosion, U absorbs several times $10^{24}$ neutrons in few nanoseconds (few moles of neutrons). Has been also produced by neutron irradiation of gram quantities of Pu in the high-flux MTR in Idaho
d	1955	$^{253}\text{Es}(\text{He}, \text{n})^{256}\text{Md}$ (EC, 1.3 d)* $^{256}\text{Md}$ gives $^{256}\text{Fm}$ (SF, 2.6 h)* $E_{\text{He}} = 35 \text{ MeV}$ , $100 \mu\text{A}/\text{cm}^2$ , Berkeley	$10^9$ atoms of $^{253}\text{Es}$ ( $\alpha$ , 20 h) produced at Idaho, $^{256}\text{Md}$ produced one atom at a time for a total of 17 atoms. Side ( $\alpha$ , n) nuclear reactions on $^{244}\text{Cm}$ giving $^{246}\text{Cf}$
e	1958	$^{246}\text{Cm}$ ( $^{12}\text{C}$ , $4\text{n}$ ) $^{254}\text{No}$ and $^{244}\text{Cm}$ ( $^{12}\text{C}$ , $4\text{n}$ ) $^{252}\text{No}$ . $^{254}\text{No}$ gives $^{250}\text{Fm}$ ( $\alpha$ , 3 s) $^{252}\text{No}$ gives $^{248}\text{Fm}$ ( $\alpha$ , 36 s) HILAC Berkeley	Berkeley group clearly identify $^{254}\text{No}$ based on the existence of $^{250}\text{Fm}$ (11 atoms detected at their correct position in elution and right $^{252}\text{No}$ nuclear decay characteristics. Other groups using $^{244}\text{Cm}$ and $^{13}\text{C}$ – Stockholm – or $^{239}\text{Pu}$ and $^{16}\text{O}$ – Dubna – did not identify reaction products. In 1964, Dubna group identified $^{256}\text{No}(\alpha, \text{n})$ as parent of $^{252}\text{Fm}$ . The existence of No was proven.
f	1961	$^{249\text{to}252}\text{Cf}(^{10, 11}\text{B}, \text{xn})^{257}\text{Lr}(\alpha, 4.3 \text{ s})$ HILAC, Berkeley	3 $\mu\text{g}$ of Cf, few atoms of $^{257}\text{Lr}$ detected among other heavy radionuclides. Existence of $^{256}\text{Lr}$ ( $\alpha$ , 45 s) confirmed in 1965 by the Dubna group as a product of $^{243}\text{Am}$ ( $^{18}\text{O}$ , $5\text{n}$ ) reaction.

All data are taken from [6].

\*EC, electronic capture, SF, spontaneous fission.

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## 5. Trends of the properties of new radioelements discovered after 1937

### 5.1. Cis-uranium

The chemical behaviours of the four radioelements discovered after 1932 are consistent with what is expected from their place in the periodic table. Only  $^{147}\text{Pm}$  ( $T_{1/2} = 2.62 \text{ y}$ ) and  $^{99}\text{Tc}$  ( $T_{1/2} = 2.10^5 \text{ y}$ ), which are fission products, can be obtained in weighable quantities. Only Tc is of interest and the isotope  $^{99}\text{Tc}$  can be more easily produced through neutron irradiation of  $^{98}\text{Mo}$  than through processing of the spent fuel. The radiative capture reaction on  $^{98}\text{Mo}$  generates  $^{99}\text{Mo}$  ( $T_{1/2} = 66 \text{ h}$ ), which decays by beta emission to the short-lived isomer of  $^{99}\text{Tc}$ :  $^{99\text{m}}\text{Tc}$  ( $T_{1/2} = 6 \text{ h}$ ). Due to its gamma emission of 300 keV,  $^{99\text{m}}\text{Tc}$  is used worldwide in nuclear medicine. Technetium has a complicated chemistry, well understood and mastered for preparing labelled bio-organic molecules [18].

### 5.2. Trans-uranium: actinides

As already said, McMillan proposed in 1941 to rank the trans-uranium elements in an “uranide series”, an idea shared by Seaborg. A few years latter (1944), Seaborg proposed to include them in an “actinide series”, corresponding to the lanthanide series. The first idea was based on the evidence that the behaviours of Np and Pu were quite different from those of Re and Os. In 1944, no experimental data was really known to base the second proposition. It was rather an ingenious intuition. The similar chemical behaviour of Ac and of Am to Lr to those of lanthanides, which is typically a chemistry of trivalent elements (except No which is divalent), confirmed this brilliant hypothesis. Nevertheless, some controversy appeared as soon as 1947 [17] because it was firmly known that the chemical behaviours of Th, Pa, and U were near that of tetravalent hafnium, pentavalent tantalum, and hexavalent tungsten, all being 5d elements. Finally, the concept of an actinide series became obvious, and today all chemists accept it.

Since the nineteen fifties a large amount of experimental and theoretical data supports the ranking of elements Ac to Lr in a series corresponding to the filling of the 5f sub-shell just as lanthanide elements correspond to the filling of the 4f sub-shell. But there is no strict correspondence in the fillings of the 4f/5f inner sub-shells because some relativistic effects occur in the binding of 5f electrons to the nucleus. Moreover, the energies of the 5f and 6d shells are closer than those of the 4f and 5d, which is the reason why the participation of 5f electrons to chemical bonding and the delocalisation of 5f electrons, for instance in the metallic state for actinides up to Am, are possible.

The chemical properties of light actinides and lanthanides are quite different. The oxidation states of the former are numerous: Th (4), Pa (4 and 5), U (3 to 6), Np (4 to 7), Pu (3 to 7), Am (3 to 6), Cm (3 and 4), and exotic low oxidation states could be prepared in molten salts, for instance. That means that U to Am actinides can make an infinity of bonds with other elements. Indeed, they have a rich and complex chemistry. In contrast, Cm and the following actinides behave as

trivalent elements, because the energy of the 5f sub-shell is lower than the energy of 6d and, consequently, the 5f electrons are less available for bonding. Their chemical behaviour is rather simple.

Among actinides, only the elements Th, U, Np, Pu, Am, and Cm are present in large quantities in natural ores (U and Th) or in neutron-irradiated uranium (e.g., spent nuclear reactor fuel). Several isotopes of actinides produced in variable quantities from grams to kilograms are used for particular applications [13].

From a historical point of view, the most important actinide element is Pu. Within the five years following its discovery, the use of Pu was to make atomic bombs. This triggered important changes for mankind. Never before, the discovery and use of an element had had such a strong impact. From a chemical point of view, Pu is maybe the element with the most complicated physical chemistry of all the elements. It displays seven allotropic forms in the metallic state and makes alloys with numerous other metals. The delta phase, stabilized at room temperature as a Pu–Ga alloy, allows us to make nuclear engines. When it reacts with other elements, it forms a variety of compounds with up to twelve coordinated bonds and numerous ionic species in solution. In certain chemical conditions, four oxidation states can exist in equilibrium [19–21].

## 6. Conclusion

The discovery of the trans-uranium elements, “actinides”, is a quite short but complicated story in which radiochemistry played a major role as well as heavy experimental means of irradiation of uranium like cyclotrons and nuclear reactors. The discovery in 1937 of three of the missing elements, which are artificial elements, has been in line with this scientific context and could not have been possible before. That of francium resulted from Marie Curie’s methodology used in the unravelling of the natural radionuclides. The period of time around 1940 has been exceptionally fertile regarding the growth of knowledge that was then utilised for the identification of minute amounts of new radionuclides, for their production in weighable amounts and for the preparation of their compounds. Plutonium is the most fascinating of the actinides discovered during World War II. Its physical and chemical properties are unique among all the elements.

Finally, the discoveries of actinides opened the way to the synthesis of the trans-lawrencium elements,  $Z = 104$  to 118. But that is another story belonging to the 1969–2002 timeline [22,23].

## Appendix. A short account of progresses of nuclear science between 1898 and 1940 from the point of view of a radiochemist

The story of the discovery of the radioelements, polonium (Po) and radium (Ra), is well known and amply documented [24,25]. Pierre and Marie Curie discovered Po and Ra in the second half of 1898, two years after the discovery of the “uranic rays” by Henri Becquerel [26]. Just one year earlier, in 1897, Johnstone Stoney and Joseph Thomson had discovered the electron as a tiny corpuscle bearing an electric negative charge. The uranic rays emitted by uranium and thorium salts blackened a photographic plate that was well protected from any excitation sources (light, electric or magnetic fields) and discharged an electroscope by ionising air, i.e. by delivering electric charges in the air. Marie Curie has supplemented these qualitative means of detection of uranic rays with quantitative ones. She has been able to measure the activity of uranic rays in term of electric current, thanks to a device from Pierre Curie, consisting of an ionising chamber associated with an ingenious compensation system based on the piezoelectric effect, discovered by Curie and his brother in 1882. It allowed, and still allows one to measure the electric charges created by the ionisation of air in a given time using only an analytical weight box (gram to kilogram) and a chronometer. The performances of this device were astonishing. It measures electric currents, in the range of a few picoamperes (pA) to a few microamperes ( $\mu$ A). Marie Curie found that pitchblende gave a more intense current (70 pA) than 1 cm<sup>2</sup> of a pure two-year-old Moissan’s metallic uranium (3 pA), and she suspected the presence of new elements contained in pitchblende. She quickly isolated and concentrated these “radio-active” elements (as she said) from the many other elements present in uranium ores. To do that, she measured the increase of activity of different chemical precipitates from acidic solutions obtained through the dissolution of hundreds of grams of pitchblende in hydrochloric acid. Po was carried down with bismuth sulphide (Bi<sub>2</sub>S<sub>3</sub>) and Ra with barium sulphate (BaSO<sub>4</sub>). Po and Ra are in minute amounts in uranium ores, about 74  $\mu$ g for <sup>210</sup>Po and 0.34 gram for <sup>226</sup>Ra per metric tonne. Marie Curie made these elements “visible” by measuring their activities, but could not give the data that at the time was necessary to characterise an element: atomic weight relative to hydrogen or spectral signature. She introduced the unit of 1 g of Ra called Curie (Ci) to measure the activity of a radioactive substance: 1 Ci is the number of disintegrations occurring per second in 1 g of Ra. Today, the unit to measure activity is the Becquerel (Bq), one disintegration per second, and 1 Ci =  $3.7 \cdot 10^{10}$  Bq; it corresponds to 1.025 grams of Ra.

Marie Curie did not seem concerned with the places of Po and Ra in the periodic table of elements at that time. At the end of 1898, 80 elements could have been arranged in an empirical periodic table of elements as shown in Table 4, which is derived from the 1869 Mendeleev classification. Dimitri Mendeleev ranked the known elements in lines and columns according to a periodic law linking their relative atomic weights to their basic inorganic chemical properties. In Table 4, elements ranked in the same column have similar chemical properties: they are homolog elements. This table is close to the one given by Mendeleev in 1875 in a paper published in the *Comptes rendus hebdomadaires des séances de l’Académie des sciences* [30] where he commented on the discovery of gallium ( $Z = 31$ ) of which he had predicted the existence in 1869 as eka-aluminium. By the way, he assigned, in this paper, a correct atomic weight for uranium (240 in place of 118). It is worth noting that in 1869 Mendeleev predicted also the possible existence of an eka-tellurium and gave some chemical

**Table 4**

Periodic table around 1898, close to the 1875 Mendeleev periodic table. All lanthanide elements gathered in the lanthanum box were discovered, but Pm and Lu. Boxes in yellow, natural missing elements (Hf and Re will be discovered in 1923 and 1925). Boxes in red, missing radioelements. In this periodic table, homolog elements in columns are separated by an unfilled box (Th is the homolog element of Hf, Ra is that of Ba, and so on). Noble gases have been discovered in 1894 (Ar) and 1898 (Ne, Kr, and Xe).

	1a	1b	1a	2b	3a	3b	4a	4b	5a	5b	6a	6b	7a	7b	8		0
1	H																He
2	Li		Be		B		C		N		O		F				Ne
3	Na		Mg		Al		Si		P		S		Cl				Ar
4	K		Ca			Sc		Ti		V		Cr		Mn	Fe	Co	Ni
		Cu		Zn	Ga		Ge		As		Se		Br				Kr
5	Rb		Sr			Y		Zr		Nb		Mo		Tc	Ru	Rh	Pd
		Ag		Cd	In		Sn		Sb		Te		I				Xe
6	Cs		Ba			La		Hf		Ta		W		Re	Os	Ir	Pt
		Au		Hg	Tl		Pb		Bi		Po		At				Rn
7	Fr		Ra			Ac		Th		Pa		U					

properties for this element still to be discovered. In 1898, considering Po as a homolog of Bi, would have given to Po an incredible atomic weight higher than that of uranium. Po was identified as the homolog element of tellurium four years after its discovery and it took radiochemists 12 years to get macroscopic amounts of Po (100 µg is enough to obtain a spectral signature). In 1907, Marie Curie gave a precise atomic weight for Ra, which was easily identified as the homolog element of Ba.

The methodology that Marie Curie used to discover Po and Ra in trace amounts and to concentrate them up to a macroscopic scale has been followed by many chemists/radiochemists in order to identify additional radioactive elements in uranium and thorium ores, and later to identify the first manmade radioactive element.

This methodology is known today as co-precipitation [7e,29]. Co-precipitation is the incorporation of an element in minute amount (like Po or Ra) in a solid phase (like bismuth sulphide or barium sulphate) formed within a solution by an element in macroscopic amounts (like Bi or Ba). The micro-component is easily detected if it is radioactive. The ratio of micro-component over macro-component is higher in the solution than in the precipitate. If all the macro-component is precipitated, the maximum of the micro-component present in solution also settles down. To enrich the solid phase in the micro-component, one has to re-dissolve the first precipitate and then to precipitate only a part of the macro-component. The repetition of this process (dissolution / partial precipitation / dissolution / partial precipitation, etc.) is called fractional co-precipitation and can lead to high degrees of enrichment, but at each step of the process a part of the micro-component is lost. For instance, starting with a precipitate of barium chloride (BaCl<sub>2</sub>) containing 10 g of Ba and 200 µg of Ra after 10 cycles of processing, and precipitating half the quantity of Ba, one obtains an enriched precipitate containing 0.1 g of Ba and 30 µg of Ra. Its specific activity has increased by 300.

In fact, such behaviour of micro- and macro-elements results from a general distribution law, which states that, in a biphasic system, each element has its own behaviour. Micro- and macro-components can be homolog elements or not. Much depends on the mechanism of the formation of the precipitate. If the micro- and macro-components are two radioactive elements, for example a short- and a long-lived isotope of a radioactive element, it is possible to co-precipitate the micro-component, but enrichment is not possible because of the same physicochemical behaviour of the two isotopes. Equations that quantify co-precipitation are given in reference [27].

The use of co-precipitation and fractional co-precipitation are rarely enlightened when one speaks about progress in nuclear science along the first half of the twentieth century. It has led, up to 1936, (1) to two major fundamental discoveries, at least from the viewpoint of chemists/radiochemists (the discoveries of many other radioactive elements belonging to the three natural radioactive families and the proof of the existence of isotopes of elements) and (2) to the preparation of highly radioactive sources of alpha particles from Po and Ra for irradiation of various targets. The use of these sources, in turn, enabled the discovery of the components of the atom (nucleus, proton, neutron) and, in combination with appropriate co-precipitation experiments, to the discovery of artificial radioactivity. The use of sources made from compounds of Po and Ra mixed with beryllium oxide, thus emitting neutrons, and the use of co-precipitation led to the discovery of the fission of uranium.

The search for new natural radioactive elements has been triggered as soon as 1899, using co-precipitation and new devices to measure radioactivity (Geiger counters, Wilson chamber...), the nature of which (alpha, beta, gamma emissions, half-life, Fajans displacement laws...) has been clarified during the ten first years of the twentieth century [28]. The first radioactive elements identified were emanations, later called radon (1899) and actinium (1901). Actinium co-precipitated with lanthanum and could be ranked in the periodic table as homolog element of lanthanum and radon, because of its chemical inertness, as the homolog element of xenon. As soon as 1910, most of the 44 radionuclides known today to be in genetic relationship with <sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th were identified. At the time, the radioactive families were denominated as uranium I, actino-uranium and thorium families, and the radionuclides were the radioactive elements looked for. Later (1935), using mass spectrometry, Arthur Dempster identified actino-uranium as <sup>235</sup>U.



The displacement laws of Casimir Fajans (alpha emission by a radioactive element shifts the daughter two places to the left in the periodic chart and beta emission one place to the right) helped to rank the radioactive elements in the periodic table. But several of them ( $^{223}\text{Ra}$ ,  $T_{1/2} = 11$  d,  $^{223}\text{Ra}$ ,  $T_{1/2} = 5.7$  y,  $^{223}\text{Ra}$ ,  $T_{1/2} = 3.6$  d) curiously occupied the same place. By the way, Frederick Soddy showed in 1910 that three new radioactive elements with clearly different half-lives were carried down with barium chloride ( $\text{BaCl}_2$ ), as did  $^{226}\text{Ra}$  ( $T_{1/2} = 1600$  y). However, it was impossible to enrich the precipitate. So, according to co-precipitation rules, they were “radioactive elements” of the same one: Ra. In 1913, Soddy named the radioactive elements with the same chemical properties and occupying the same place in the periodic chart “isotopes”. At the same time Joseph John Thomson showed by mass spectrometry that a non-radioactive element, neon, had also isotopes. The concept of isotopes remains the most important consequence of the discovery of radioactivity. Protactinium was the last radioactive element ranked in the periodic chart in 1918. No new radioactive element was discovered before 1937.

The model of what could be an atom progressed from 1903 to 1909/1911 when Hans Geiger, Ernest Marsden, and Ernest Rutherford proved the existence of the nucleus of atom thanks to the use of an intense source (50 mCi) derived from Ra. It was a short half-life source, obtained by collecting radon (Rn), the gaseous decay of Ra called radon source. It emitted three groups of alpha particles of which one was of high energy. Ten years later (1919), Rutherford showed that the nuclei of the nitrogen atom (N) contain nuclei of hydrogen, which he named proton. The activity of the Rn source was 1 mCi and about 100 protons/min were ejected from the nucleus of the  $^{14}\text{N}$  atom. In 1913, it was recognised that elements could be arranged in a periodic table according to the charge of the nucleus. More than ten years later, in 1932, James Chadwick likewise used a Rn source (1 mCi) when he discovered the neutron by irradiating beryllium with alpha particles. The atoms appeared then definitively constituted of a nucleus containing  $Z$  protons and  $N$  neutrons surrounded by  $Z$  electrons. Since this date the elements were ranked according to  $Z$  in the periodic table, each box containing all the isotopes with different  $N$  values. The concept of elements composed of various isotopes was explained and the concept of the mole with the determination of the Avogadro number was firmly established. The distinction between elements, isotopes, radioelements, and radionuclides became widely accepted. What had so far had been called “radioactive elements” were radioactive isotopes, i.e. radionuclides. In 1932, the vacant places before U in the periodic table were  $Z = 43$  (Tc), 61 (Pm), 85 (At), and 87 (Fr).

In 1932, Carl Anderson discovered the positive electron. Two years later, Irène and Frédéric Joliot irradiated a foil of  $^{27}\text{Al}$  with a Po source of 100 mCi (the most intense source ever prepared) and found that a new radionuclide,  $^{30}\text{P}$  was quickly decaying ( $T_{1/2} = 3$  min) by emission of a positive electron (beta-plus emission). He gave proof of  $^{30}\text{P}$  production through its co-precipitation with calcium phosphate and co-evaporation with red phosphorus as gaseous phosphine.  $^{30}\text{P}$  is the first artificial radionuclide produced. The discovery of artificial radioactivity opened up a tremendous new field for research. Enrico Fermi showed that irradiation of a given radionuclide ( $Z$  protons,  $N$  neutrons) with neutrons and particularly slow neutrons could create an artificial radionuclide ( $Z$  protons,  $N + 1$  neutrons) decaying by beta emission. The daughter is a radionuclide ( $Z + 1$  protons,  $N$  neutrons) belonging to the next higher element with respect to the irradiated one. In three years, more than 200 artificial radionuclides have been identified using various radiation sources of high activities. The idea that irradiation of U with neutrons could give trans-uranium elements led in fact to the discovery of the fission of uranium. Indeed, irradiating uranium with neutrons (sources of around 1 Ci of mixed salts of Po or Ra with oxide of beryllium) produced a lot of “new radioactivities”. Otto Hahn, looking at the presence of a supposed radionuclide of Ra, found effectively that Ba co-precipitated a radioactive emitter ( $T_{1/2} = 23$  min), but it was impossible to increase the radioactivity of the precipitate, i.e. to enrich it with radium. In a complementary experiment he showed that the short-lived  $^{228}\text{Ra}$  in minute amount was co-precipitated with Ba and that the precipitate could be enriched with  $^{228}\text{Ra}$ . Hahn concluded that the 23-min activity measured in the co-precipitate was indeed a barium radionuclide and that this could only be explained by the hypothesis that the uranium nucleus could break up when irradiated with neutrons. This was the time when the fission of uranium was being discovered. The identification of hundreds of radionuclides, isotopes of 30 chemical elements formed in the fission process of  $^{235}\text{U}$ , was a Herculean accomplishment for radiochemists. Trans-uranium elements will be discovered soon after the discovery of uranium fission.

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