FROM POLONIUM TO ARTIFICIAL RADIOISOTOPES IN THE 1930'S*

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The word "radioactive" appeared for the first time in Pierre and Marie Curie's paper announcing the discovery of Polonium. Starting with the memory of this seminal event and the discovery of Radium, we focus on a few of the tremendous successes achieved in the 30's, namely the successive discoveries of the neutron and the positive electron, followed by the discoveries of artificial radioactivity and later of fission. Experimentalists were confronted with many problems as their interest shifted from radioactivity to "artificial disintegration" and cosmic rays experiments. The first discovered β^+ radioactive isotopes, ^{30}P and ^{13}N, and the first fission produced nuclei appear as early steps towards the quest for more and more exotic nuclei.

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1. Introduction

The word "radioactive" appeared for the first time in Pierre and Marie Curie's paper announcing the discovery of Polonium in July 1898. Two years before, Henri Becquerel had discovered the so called "uranic rays" [1]. He wanted to check a possible emission of X-rays by a phosphorescent salt. The crystal used in his experiments was a double sulfate of Uranium and Potassium and the result, quite unexpected, pointed to the spontaneous and continuous emission of a weak radiation by Uranium. The radiation was detected using a photographic plate. Further experiments comparing Uranium and Uranium salt radiations were performed with a crude electroscope. Becquerel then shifted to a supposedly more interesting subject. In fact, the interest of most scientists in the new rays had faded. Notable exceptions were Pierre and Marie Curie and Ernest Rutherford.

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2. The discovery of Polonium

The young Maria Skłodowska had left her native Poland to follow brilliant university studies in Paris. She had married Pierre Curie in July 1895, deciding to remain and live in France. Pierre Curie was an already well known physicist, for his works on piezoelectricity, magnetism and symmetry laws. He was a professor at the School for Physics and Chemistry in Paris. By the end of 1897, Marie Curie undertook there her experiments on Becquerel's rays, a subject which seemed suitable for a thesis.

A quantitative method was needed to go farther than Becquerel's results. The experimental device set up by Pierre Curie is schematized in Fig. 1. A powder to be studied is spread on the lower plate of a crude ionization chamber. The charges collected on the upper plate are compensated by opposite charges obtained by applying progressively a weight to the piezoelectric quartz. The compensation is continuously controlled by the electrometer. The absolute value of the ionization current could be calculated knowing the weight applied and the time during which the compensation could be maintained. The setting of the equipment was painful and humidity was a serious problem in an uncomfortable laboratory.

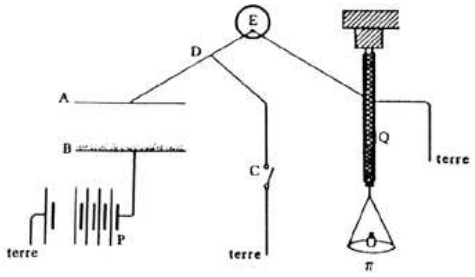

Fig. 1. Scheme of Pierre and Marie Curie's experimental set up (from Marie Curie's thesis). A, B ionization chamber plates, E electrometer, Q piezoelectric quartz.

2.1. Maria Skłodowska-Curie first note

Marie Curie focused first on the study of Uranium metal and Uranium compounds. The apparatus played an important role in her successful experiments. Her care for the ray penetration in matter was no less important. Nothing was known on the question. After some measurements performed as function of the sample thickness, she used to spread her samples in similar thin layers. Her measurements unambiguously confirmed that the emission of uranic rays was an atomic property, quite independent of the chemical or physical state. She could then concentrate on further experiments in order to answer a question of paramount importance: was the spontaneous emission of radiation by Uranium a more general phenomenon?

Her systematic search for Becquerel's rays in elements, salts, oxides and even minerals was mainly negative, with two major exceptions: she found that Thorium emitted a spontaneous and more energetic radiation than Uranium, not being aware of Schmidt observations [2]. Pitchblende and other uranium minerals exhibited a very strange behavior: they emitted more radiation than expected from their Uranium content. Careful checks confirmed the astonishing result. An artificial chalcolite prepared with ordinary chemical products exhibited on the contrary no radiation excess.

Her note to the French Academy of Sciences in April 1898 [3] put forward a possible explanation: "... the minerals may contain an element much more active than Uranium". Pierre Curie had already contributed to the research progresses. He decided to give up his own researches on crystal growth and to join Marie on the search for the unknown element.

2.2. Polonium

The success came from the tight combination of chemistry methods with activity measurements. The Curies had no idea about the concentration nor about the chemical properties of the element they were searching for. We can estimate today, that there were some 30 μg of Radium and 9 ng of Polonium in the 100 g sample of Pitchblende they were studying. They started with classical analytical chemistry searches. They quickly convinced themselves that the concentration of the unknown element was so small in the sample that only radiation measurements were able to "trace" it among the different separates resulting of chemical processes. This was the foundation of a new method of chemical analysis, the beginning of Radiochemistry. They are shown in Fig. 2 with their electrometric set-up. Marie is handling the weight that exerts a slowly increasing traction on the Quartz. The handling required considerable skill.

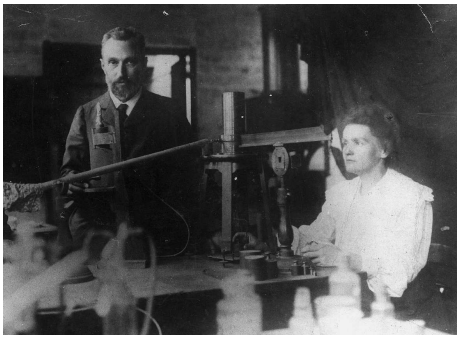

Fig. 2. Pierre and Marie Curie with their electrometric set-up (Curie and Joliot-Curie archives).

It is not the purpose here to describe the different separation steps leading to the discovery of Polonium. As clear from the note book, both Marie and Pierre performed chemical separations and activity measurements, developing several attempts in parallel or combining their efforts on a same delicate operation. At the end, they obtained a substance 400 times more active than Uranium by applying the sublimation method studied mostly by Pierre Curie to the sulfide separates concentrated by Marie at a result of different chemical steps. The Curie announced the discovery of Polonium in July 1898 [4]. "We believe that the substance we recovered from pitchblende contains an heretofore unknown metal, similar to Bismuth in its analytical properties. If the existence of this new element is confirmed, we propose that it be named Polonium in honor of the native land of one of us".

The choice of the name Polonium had clearly a provocative significance as Poland was parceled out at that time.

No spectral line could be attributed to the new element, which concentration in the sample was too small. The existence of an invisible element which could be identified solely on the basis of its radiation emission was claimed for the first time. Polonium remained thus for several years a much debated subject. Radioactivity was thought at the beginning a spontaneous phenomenon constant in time. Doubts emerged about the nature of Polonium when Marie observed that the activity of her samples decreased: was Polonium only a kind of "active Bismuth"? Later the discovery of a radioelement with chemical properties of Tellurium was claimed. Marie Curie proved its identity with Polonium. Polonium could only be produced in macroscopic amount in the forties.

The situation was quite different for the second element Radium discovered by the Curie six months after Polonium with the collaboration of the chemist G. Bémont [5]. It was possible to concentrate Radium by fractional crystallization of Barium chloride. The Radium chloride concentration in Barium chloride salts, in spite of being tiny, was large enough to allow the observation of until then unknown spectral lines the intensity of which followed the sample activity. Most physicists recognized this as a robust proof for the new element. Marie Curie gave the chemical proof for the existence of Radium by the measurement of its atomic weight. Starting with tons of pitchblende residues, she successfully prepared the necessary amount of pure Radium chloride.

Radium played by far a more important role than Polonium. Its separation in significant amount opened the way to its medical and industrial application, in addition to its use in laboratories. Polonium sources, however, became especially popular in the thirties, as their monoenergetic alpha rays were best suited for the study of transmutation processes.

3. Radioactivity and nuclear physics in the thirties

3.1. The Solvay Council of Physics

The Solvay Council of Physics held in October 1933 in Brussels is most representative of the years thirties. The Council gathered an impressive number of present and future Nobel Prize winners, as shown in the picture in Fig. 3. The old generation was present, Rutherford and Marie Curie, as well as the intermediate one, Niels Bohr, Lise Meitner or James Chadwick. Younger physicists, such as Pauli, Heisenberg or Oppenheimer, Fermi, Lawrence or the Joliot-Curie among others had already published important results.

Fig. 3. Participants to the Solvay Council of Physics in October 1933 (Curie and Joliot-Curie archives).

The status of theory was very different from the present one. Most physicists believed following Rutherford opinion that the role of theory was to explain experimental facts, not to predict unknown ones. Quantum mechanics applied to nuclear physics was still in its infancy. Experiment remained the main driving force in the thirties on the way from radioactivity to nuclear physics.

The nucleus had been discovered in 1911, nuclear transmutations also called artificial disintegrations in 1919, the Compton effect in 1923. The families of natural radioisotopes were nearly completely known. In spite of theses successes, many problems remained open by the end of the twenties. Accelerators were still at the stage of exploration. Detection methods were generally not selective enough for studying the few particles produced by artificial disintegrations among what physicists happened to call a "soup of radiation", radiation of primary particles and secondary ones resulting of atomic processes. Among the open problems, the nucleus composition, the

continuous nature of beta spectra, definitely recognized but a subject of hard controversies, the anomalous absorption of high energy gamma rays, not account for by the Compton effect.

A conference held in Rome in 1931 gathered nuclear physicists and cosmic rays physicists. It seems retrospectively as giving the signal of the discoveries to come with the marvelous year 1932: the discovery of Deuterium, of the neutron and of the positive electron. The discussions opposed Bohr and Pauli about a possible non conservation of energy in beta decay, Millikan against Bothe and Rossi about the nature of cosmic rays, gamma rays or particles [6]. Physicists were puzzled by the highly penetrating radiation recently discovered in nuclear reactions and they wondered it could also be found in cosmic rays.

3.2. The discovery of the neutron

In August 1930 W. Bothe and H. Becker in Berlin reported that Polonium α particles produced a weak emission of penetrating rays on several light elements, in particular Beryllium and Boron [7]. The Radium Institute with the Joliot-Curie, and the Cambridge Laboratory, especially with Webster, became interested in the subject.

Webster started experiments using a high pressure ionization chamber in order to increase the sensitivity to penetrating rays. Webster indeed improved the results obtained in Berlin, but did not find any significant new feature of the radiation. The Joliot-Curie's approach was completely different. It allowed them to discover that the Bothe and Becker radiation projected out high speed protons from hydrogenous substances.

3.3. A property of the Bothe and Becker radiation

The Joliot-Curie prepared especially powerful Polonium sources for their experiments, with activities as high as 200 millicuries. The set up used is schematized in Fig. 4. The α particles emitted by the Polonium source at the upper part of the device bombarded a foil of Lithium, Beryllium or Boron, placed immediately below. Screens of different thicknesses and compositions could be placed in front of the ionization chamber connected to a very sensitive electrometer. The ionization chamber operated at normal pressure and it was closed by a thin aluminum window. The idea behind this latter choice was that a possible secondary radiation, with unknown absorption properties, would thus not be missed. It was rewarding.

The Joliot-Curie started to study the absorption properties of the radiation produced in Beryllium, using different materials for the absorber foil. It was a big surprise to observe the significant increase of the ionization current with a screen made of paraffin. The same behavior was found with all other substances containing significant amount of Hydrogen. Absorption

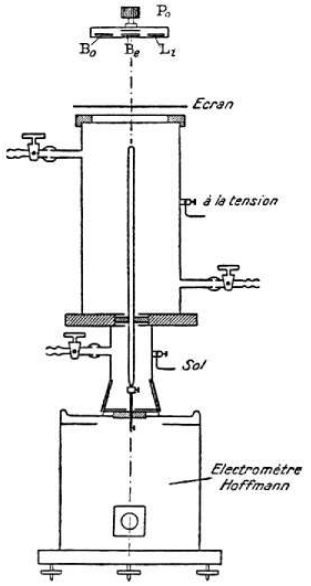

Fig. 4. Set-up of Curie and Joliot's experiment (from I. Curie, F. Joliot, *J. Phys. Rad.* **4**, 21 (1933)).

measurements of the secondary radiation identified it beyond any doubts as protons of several MeV. The results on Beryllium and Boron were rapidly published, in mid January 1932 [8]. In their note, the authors suggested a kind of Compton effect on protons, without bothering about the very high energy of the supposed penetrating rays that the hypothesis implied, which contradicted the absorption measurements and moreover the conservation of energy in the reaction.

It is said that Rutherford, reading the Paris note, exclaimed "I don't believe that". Chadwick checked and confirmed the results. A much attractive hypothesis to explain them was already roaming in the Cavendish Laboratory since Rutherford's Bakarian lecture, 10 years before: the existence of a neutral particle, a tightly bound combination of a proton and an electron.

3.4. Chadwick's decisive experiments

The set up of Chadwick's decisive experiments is schematized in Fig. 5. The Polonium source and the Beryllium or Boron plates were enclosed in a vacuum chamber. The produced radiation traveled to the paraffin foil, clearly identified as a converter. The ejected protons could be measured individually, as the ionization chamber was connected to an amplifier and the induced pulses were recorded by an oscillograph. This was a decisive improvement compared with the integral measurements of the Joliot.

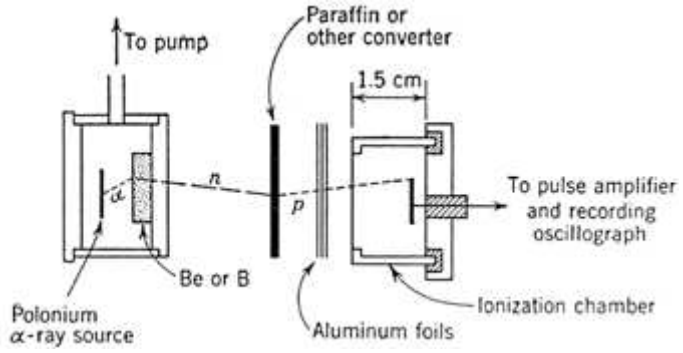

Fig. 5. Set-up of Chadwick's experiment (from J. Chadwick, *Proc. Roy. Soc* **136**, 692 (1932)).

The proton absorption was carefully studied for two orientations of the source vessel. Chadwick also performed experiments with converters of light elements placed very near the chamber. Recoil nuclei were observed. All results, in the different kinematics, pointed to the same conclusion: the Bothe and Becker radiation is a neutral particle with approximately the proton mass. The discovery of the neutron was published by J. Chadwick in a short note in Nature [9]. In spite of all the evidences in favor of the neutron enumerated in the paper, the conclusion of Chadwick's short note is the following: "It is to be expected that many of the effects of a neutron in passing through matter should resemble those of a quantum of high energy, and it is not easy to reach the final decision between the two hypotheses. Up to the present, all the evidence is in favor of the neutron, while the quantum hypothesis can only be upheld if the conservation of energy and momentum be relinquished at some point".

In fact, both neutrons and gamma rays were produced in Joliot-Curie and Chadwick's experiments, neutrons being responsible of the observed proton or nucleus recoils. But electrons also reached the ionization chambers. The discovery of the pair effect and of artificial radioactivity will settle the unresolved questions in the next two years. In the mean time the positive electron had been discovered in cosmic rays.

3.5. Discovery of the positive electron

Already before the Rome conference, Anderson and Millikan had started building a large cloud chamber, equipped with coils producing an axial magnetic field. The chamber was a vertical one, a choice suitable for studying radiation coming from out space to the earth. Anderson decided to dispose a lead plate horizontally inside the chamber.

He started a systematic investigation and soon recorded a strange cosmic ray track such as the one shown in Fig. 6. The track thickness resembled that of an electron, the responsible particle could not be a proton. Nevertheless, taking into account the direction of the track curvature and its change at the crossing of the lead plate, the particle was a positive one. Anderson was not aware of Dirac's prediction. One understands he was especially careful about a possible experimental mistake before publishing his result in August 1932 [10]. The existence of positrons was soon confirmed and not only in cosmic rays. Several physicists, especially the Joliot-Curie remembered of strange electron trajectories, attributed to Compton electrons bouncing back from cloud chamber walls, which was the case for only part of them.

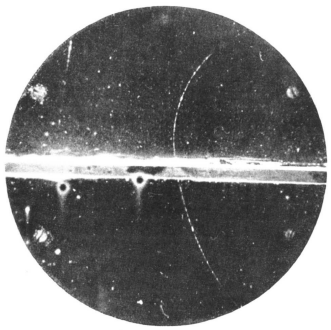

Fig. 6. Positive electron track in Anderson cloud chamber (from C.D. Anderson, *Phys. Rev.* **43**, 491 (1933)).

New experiments demonstrated that positrons could also be produced by high energy gamma rays. The pair creation effect answered the old question of gamma ray anomalous absorption. Positron annihilation was observed, confirming Dirac's prediction.

3.6. The discovery of artificial radioactivity

During the years 1932–1933, the study of neutron producing reactions remained a main subject of interest, in addition to positrons. It is the intertwining of experiments bearing on the two subjects, which led the Joliot-Curie to the discovery of artificial radioactivity.

They concentrated on the study of reactions induced by Polonium alpha rays on Boron and especially Aluminum. Experiments on Aluminum led them to the observation of neutrons, a quite surprising result as no reasonable reaction process seemed able to explain the fact. An even more surprising result was the observation of swift positive electrons, as shown in the cloud chamber photography shown in Fig. 7. The simplest assumption was to attribute it to pair creation by gamma rays, but the number and

energies of positive electrons were found significantly too large, as compared with those of negative electrons. The proton track shown in Fig. 7 was on the contrary easily explained by the (α, p) reaction on Al. The Joliot-Curie dared to assume that, in certain cases, a neutron was emitted together with a positive electron, instead of a proton thus leading to the same ^{30}Si residual nucleus. They presented their results at the Solvay Council in October 1933. The supposed existence of "transmutation positrons" was strongly criticized. The experimental results were considered not so reliable, as Lise Meitner stated that she had not observed neutrons with an Aluminum target. As related by the Joliot-Curie later, Bohr and Pauli encouraged them privately with a comment like: "We don't understand, but there is something important behind".

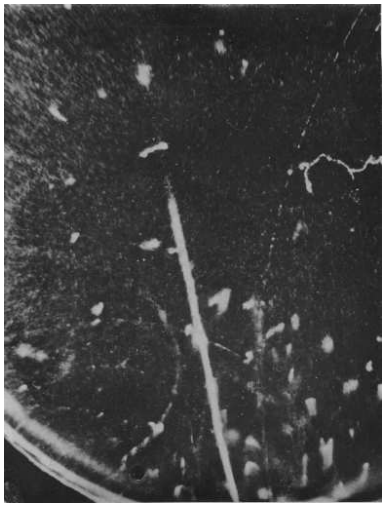

Fig. 7. Proton and positive electron produced in Aluminum (from I. Curie, F. Joliot, *Act. Scien. Ind.* **182** (1934) Hermann, editor).

Coming back to Paris, the team started comparing carefully the neutron and the positron reaction thresholds. The experimental method is schematized in Fig. 8. The positrons were detected with a Geiger counter, and the neutrons were measured with an ionization chamber with paraffin covered walls. The energy of the α particles impinging the Aluminum window used as a target was adjusted by changing the pressure in the vessel. Neutron and Positron thresholds were found the same. One more experiment with the Geiger counter, gave the clue. Starting a measurement immediately after increasing the pressure below the threshold, the "background" counting rate was found much higher than previously obtained and decreasing with time.

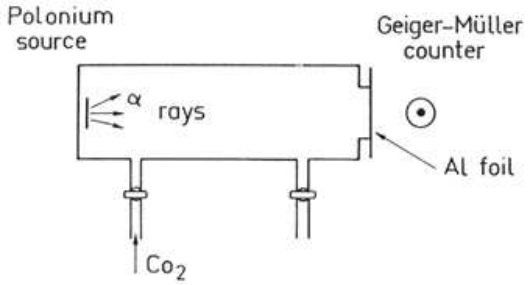

Fig. 8. Set-up for the determination of positron emission thresholds.

The decisive experiment was incredibly simple, except for the delicate counter operation. An Aluminum foil irradiated for 10 minutes, was taken near the counter away from the source. The exponentially decaying counting rate showed that a radioactive isotope had been undoubtedly produced. All observations could be easily explained assuming the process occurred in two steps. The reaction of alpha particles on aluminum had nothing special, except that it produced a radioactive residual nucleus ^{30}P, instead of a known stable nucleus. A similar conclusion was reached with a Boron target, leading to the residual nucleus ^{13}N. Before the experimental evidence, nobody had thought that stable nuclei were not the only ones possible.

The discovery of artificial radioactivity was at the same time a discovery of a new type of radioactivity, by emission of a positive electron. The paper on the new type of radioactivity was published on January 15th, 1934 [11]. Nearly at the same time, Enrico Fermi published his theory of beta radioactivity in an Italian review. A shorter version of that paper had been rejected by the well-known journal Nature. Positron radioactivity was soon included in the Fermi's theory. Two weeks after their first paper, the Joliot-Curie published the chemical proofs of the transformation of Aluminum in Phosphorus and of Boron in Nitrogen [12]. The rapid chemical separations were achieved in 10 cm high glass devices blown by Joliot himself, such as the one schematized in Fig. 9.

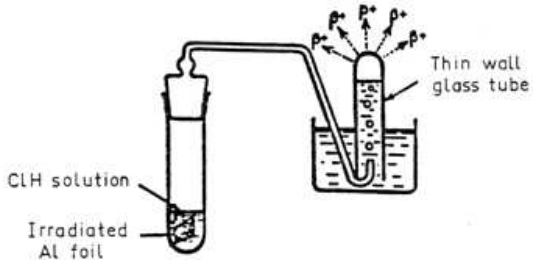

Fig. 9. Chemical separation of ^{30}P.

Artificial radioactivity was easy to confirm. One of the firsts to do so was Lawrence at Berkeley with the deuteron beam of his recently built cyclotron. The nuclear chart was rapidly enriched with dozen of radioisotopes. Fermi immediately understood the great advantage of neutrons for their production in heavy elements.

3.7. The discovery of fission

Fermi and his group undertook a systematic search of new radioisotopes via (n, γ) reactions using more and more heavy targets. Quite naturally, they expected that the irradiation of an Uranium target would produce Uranium isotopes decaying via β-radioactivity to an isotope of a transuranic element with atomic number 93. The concept seemed to work, even too well. Fermi discovered not one but five new activities [13]. Chemical identification of the supposed transuranic elements was, however, quite difficult. The subject shifted to the Berlin group in the following years. O. Hahn, L. Meitner and F. Strassman had the best expertise in radiochemistry in addition to nuclear physics.

The part of interest of the periodic table, as known in the thirties is shown in Fig. 10. Under those conditions, possible transuranic elements of atomic number 93, 94, and 95 were expected to exhibit chemical properties similar to Rhenium, Platinum and Osmium, and so on. This was a misleading deduction. In modern tables, Actinium and the following elements, the actinides, occupy only one place, just as all rare earth elements are located at the Lanthanum place.

O. Hahn, L. Meitner and F. Strassman discovered a number of new activities characterized by their half lives, in addition to those of Fermi. They attempted to organize them, taking into account the supposed chemical similarities [14]. The different activities were attributed to four transuranic elements, chains of isotopes and groups of isomers linked by their β-decay.

Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46
Ba 56	La 57 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78
Ra 88	Ac 89	Th 90	Pa 91	U 92	93	94	95	96

Fig. 10. Periodic table in the thirties and transuranic elements.

Irene Curie in Paris entered the competition in 1937, with her collaborator Paul Savich. They adopted a new approach to the problem, using absorbers to select the most energetic beta emitters. This allowed larger irradiation times, and as a consequence the discovery of a new beta activity with the relatively large half life of 3.5 hours. All efforts were then concentrated on the chemical identification of the element responsible for that radioactivity, assuming as in Berlin that it could only be an element nearby Uranium. The detailed story is too long. Chemical separation procedures were systematically tested, and different assumptions were rejected. A controversy started with Hahn, irritated by this radioactivity which did not fit the Berlin interpretation. For him Irene Curie was a physicist, not a chemist, she was working with the methods used 40 years ago by her mother. The main conclusion of I. Curie and P. Savitch paper in October 1938 [15] led them very near the discovery of fission: "the properties of R 3.5 hours are those of Lanthanum from which it seems it can only be separated by fractionation". It turned to be correct. It was understood later that traces of radioyttrium with similar chemical properties were present together with the Lanthanum fission product.

The details of the Paris paper convinced F. Strassman (L. Meitner had successfully escaped from Germany in July) that they must be taken seriously. Otto Hahn finally decided to undertake new experiments. The 3.5 hours activity was confirmed and attributed at first to Actinium isotopes produced via beta decay of Radium isomers. The next step was to focus on the identification of activities they had previously attributed to such Radium isomers. Fractional crystallizations, similar to Marie Curie's method forced them to attribute their products not to Radium, as expected, but to Baryum. O. Hahn and F. Strassman submitted their famous paper by the end of December 1938 [16] with the following statement: "We must name Barium, Lanthanum and Cerium, what we called previously Radium, Actinium and Thorium. This is a difficult decision, which contradicts all previous nuclear physics experiments".

The first artificial radioisotopes and the first fission produced radioactive nuclei opened the way to the study of nuclear matter away from the stability line. They are the ancestors of our modern exotic nuclei.

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