

## Francium (Atomic Number 87), the Last Discovered Natural Element

Jean-Pierre Adloff† and George B. Kauffman\*

Université Louis Pasteur, 63 Rue Saint Urbain, Strasbourg, France F-67100, jpadloff@noos.fr and Department of Chemistry, California State University, Fresno, Fresno, CA 93740-8034, georgek@csufresno.edu

**Abstract:** In 1935 the three natural radioactive series ( $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ ) were coherent and complete, but the elements with atomic numbers 85 and 87 were still missing in the periodic table. It was anticipated that an isotope of element 87 could be formed by  $\alpha$ -decay of actinium. In 1939 a young technician, Marguerite Perey (1909–1975), the 30th anniversary of whose death we celebrate this year, was recruited at the Institut du Radium in Paris as the personal laboratory assistant of Marie Curie (1867–1934). For many years Perey worked on actinium and in 1939 discovered the first isotope of element 87, Dmitrii Ivanovich Mendeleev's eka-cesium, the heaviest alkali metal, for which she proposed the name "francium." The events leading up to Perey's discovery, her work, and its consequences are recounted.

## Introduction

One of the most impressive successes of the new science of radiochemistry was the discovery within 15 years of five elements with atomic numbers between 84 and 91 for which Dmitrii Ivanovich Mendeleev (1834–1907) had allotted places in his periodic chart—polonium (84), radon (86), radium (88), actinium (89), and protactinium (91). These elements shared with uranium (92) and thorium (90) the property of spontaneous emission of radiation. Thus it could be predicted with little risk that *all* the elements with atomic numbers beyond 83 would be radioactive. This would be the case for element 87, the heaviest alkali metal element, *eka-cesium* in Mendeleev's terminology.

It is amazing that the search for a *stable* eka-Cs was nevertheless attempted even after the discovery of artificial radioactivity in 1934. Pseudo-discoveries of *russium* (1925), *alcalinium* (1929), and *virginium* (1932) (simultaneously with that of element 85, *alabamine*) in minerals and natural concentrates containing heavy alkali metals were reported [1–3]. Occasionally, it was concluded that elements 85 and 87 could not exist at all [4].

The last claim for a stable element 87 appeared in 1936. Horia Hulubei (1896–1972), a Romanian investigator in the laboratory of the distinguished physicist and 1926 Nobel physics laureate Jean Perrin (1870–1942) in Paris, announced that he had detected in a sample of lepidolite, a lithium mica ((OH,F) $_2$ KLiAl $_2$ Si $_3$ O $_{10}$ ), the  $L\alpha_1$  and  $L\alpha_2$  lines of eka-Cs with wavelengths close to those predicted by Henry Gwyn Jeffreys Moseley's (1887–1915) law [5]. Hulubei emphasized that the discovered element was "not fugitive," by which he probably meant that it was stable rather than radioactive. A year later, in a second publication, he added, "these results [the  $L\alpha$  lines] strengthen my first results on element 87, although the weakness of the observed emissions emphasizes its rarity." He proposed the name *moldavium* with symbol MI, for the province of Moldavia in his native Romania [6]. For obscure reasons Jean Perrin strongly supported Hulubei's claim. The

controversy lasted for several years, even after the actual discovery of eka-Cs [7].

## The Search for Radioactive Eka-Cesium

During the mid-1930s no major discovery in the field of natural radioelements was anticipated as much as that of element 87, especially since in 1934 artificial radioactivity had opened wide opportunities for research in radiochemistry. The three radioactive series, headed by  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ , were coherent and presumably complete. The elements 87 and 85 were missing either because they might belong to a fourth, still unknown series or be hidden in one of the three series.

The search for a radioactive element 87 in the natural radioactive series was not attempted until the radioactive displacement laws had been established. In 1913 the unraveling of the complex mixtures of radioactive substances formed in the decay of radium, thorium, and actinium had reached a point where the systematics of radioactive transformation became evident. Two simple rules were established: (1) If a radioelement emits an  $\alpha$ -particle, its decay product is shifted two places to the left in the periodic table, and (2) If it emits a  $\beta$ -particle, the decay product is shifted one place to the right. It was now trivial that an isotope of element 87 could be formed directly only in the  $\alpha$ -decay of element 89 (actinium) or the  $\beta$ -decay of an isotope of element 86 (radon):



The actinium isotopes were  $\beta$ -emitters, and the radon isotopes decayed with emission of  $\alpha$ -particles. On the other hand, dual decay processes by emission of  $\alpha$ - and  $\beta$ -particles from the *same* isotope were already known in the three series. Accordingly, either actinium or radon isotopes might well disintegrate into an isotope of eka-Cs. These considerations stimulated the search for eka-Cs. With few exceptions, reported trials dealt with actinium, perhaps owing to experimental difficulties or to a premonition that the search with emanations would be vain. Today the  $\beta$ -decay of the three natural radon isotopes is definitively excluded. Therefore the search for eka-Cs was concentrated on actinium.

\* Series Editor contribution

† Marguerite Perey's first research student and successor



Figure 1. André Louis Debierne (1874–1949), about 1901.

### Actinium [8]

In 1900 André Louis Debierne (1874–1949) (Figure 1), the collaborator of Pierre Curie (1859–1906) and Marie Curie, announced the discovery of a thorium-like element, which he named *actinium*. The name from the Greek *ακτις*, *ακτινος*, “ray,” was illogical because actinium scarcely emits any observable radiation. Actinium was the third radioelement found in uranium ores after polonium and radium. Four years later, the German radiochemist Friedrich Oskar Giesel (1852–1927) claimed the discovery of a new element, *emanium*, a strongly radioactive substance, closely similar to the rare earth lanthanum (atomic number 57). In this respect he was correct, and a long controversy followed concerning the priority of the discovery. This question is still equivocal although Debierne is now officially recognized as the discoverer, and consequently the name *actinium* was retained. Neither of the two authors indicated the half-life of their product.

In 1908 Otto Hahn (1879–1968) found in thorium compounds a radioactive substance, which he named *mesothorium 2* with the symbol  $\text{MsTh}_2$  [9]. The esoteric names of the numerous radioactive substances discovered during the early history of radiochemistry (for example,  $\text{AcA}$  is polonium,  $\text{AcX}$  is radium,  $\text{AcC}''$  is thallium, radioactinium is thorium, etc.) may confuse a person unfamiliar with the original literature. For easier comprehension, these names are converted into the usual denomination of nuclides. In this system  $\text{MsTh}_2$  is  $^{228}\text{Ac}$ , the second natural isotope of the element after Debierne's  $^{227}\text{Ac}$ .

$^{228}\text{Ac}$  is a  $\beta$ -emitter with a very convenient half-life of about 6 hours, and it is more easily handled, purified, and measured than  $^{227}\text{Ac}$ . It was a prime candidate as the parent of  $^{224}\text{Eka-Cs}$ . The experiment required two proofs: (1) the detection of the  $\alpha$ -radiation of the parent nuclide and (2) the measurement of the daughter nuclide and its identification as an alkali metal element. These two conditions would be fulfilled only in the actual discovery of element 87.

In 1926, after a vain search for a stable radium (eka-barium), Hahn found it exciting to pursue the search for eka-Cs [10]. The procedure was based on the precipitation of mixed crystals of cesium and eka-Cs hexachloroplatinate(IV) from a very active solution of the trivalent  $^{228}\text{Ac}$  after thorough elimination of all known daughter products. The result was negative. The estimated  $\alpha$ -branching of  $^{228}\text{Ac}$  was less than  $10^{-8}$ . Other claims for  $\alpha$ -decay of  $^{228}\text{Ac}$  were not confirmed [1]. In recent

tables of nuclides the  $\alpha$ -decay of  $^{228}\text{Ac}$  is ignored or reported as very weak and with a question mark.

After the deceptive experiment with  $^{228}\text{Ac}$ , Hahn commented that the next logical step would have been a similar trial with  $^{227}\text{Ac}$ :

Curiously, I did not perform the experiment although in my previous works with actinium I never succeeded in the preparation of really inactive actinium (*wirklich inaktives Actinium*) [Hahn meant that without a slight residual  $\alpha$ -activity, the  $\beta$ -emission of actinium itself was not measurable; see below]. I was not confident enough in my method for purifying actinium [10].

Hahn ascribed the residual activity to traces of  $^{227}\text{Th}$ , the first descendant of  $^{227}\text{Ac}$ . However, he added that if this radiation really belonged to actinium, it would be of the order of only 0.2 to 0.3 percent of the maximum activity at equilibrium. Indeed, as we shall see, the percentage of  $^{227}\text{Ac}$ 's initial and own  $\alpha$ -activity is 1.2 percent. Hahn was close to the discovery of eka-Cs, an accomplishment that would not have been a surprise, owing to his prodigious achievements in a lifetime dedicated to radiochemistry that was crowned in 1944 with the Nobel Prize for Chemistry.

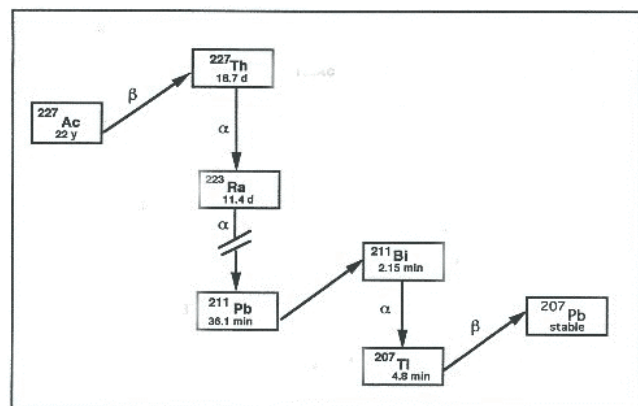
In 1914 the Vienna group of Stefan Meyer, Viktor F. Hess, and Friedrich Adolf Paneth (1887–1958) undertook careful measurements of the range of  $\alpha$ -particles of various substances, including Hahn's “residual radiation” [11]. The purified  $^{227}\text{Ac}$  emitted  $\alpha$ -particles with a range in air of 3.4 cm. and a very small intensity. Although the measurement was not very precise, because of the in-growth of daughter products, the range was significantly shorter than that of any substance in the actinium series. Application of the Geiger–Nuttall rule led to an estimated 130-year half-life for the emitter. The researchers wondered if still unknown elements were present in the actinium series. The work was interrupted by the outbreak of World War I less than one month after their report. The observation of  $\alpha$ -particles with a 3.4-cm. range was subject to considerable doubt during the next twenty years, since it seemed possible that the new particles could be ascribed to daughters of actinium or to  $^{231}\text{Pa}$ , the parent of  $^{227}\text{Ac}$ , discovered in 1918, whose own radiation had a range of 3.54 cm. In fact, the team had probably measured, without knowing it, the long-sought  $\alpha$ -radiation from  $^{227}\text{Ac}$  to  $^{223}\text{Eka-Cs}$ .

### The Actinium Puzzle

For years actinium remained a barren subject. Ten years after the discovery, the properties of the element could be described mostly in negative terms—atomic weight, unknown; half-life, unknown; radiation emitted, none; precursor, unknown. In 1930 the data on actinium had improved, but it was still the least scrutinized radioelement. The investigation of actinium was hampered for several reasons: (1) The equilibrium ratio of actinium in uranium is very small ( $0.21 \times 10^{-9}$ ). The amount of  $^{227}\text{Ac}$  in pitchblende, the main uranium ore, is  $0.6 \times 10^{-3}$  that of radium. (2) As noted by Giesel, the chemical properties of actinium are close to those of the rare earths, which are contained in considerable amounts in pitchblende. In the extraction procedures actinium is always mixed with these elements, in particular with lanthanum, its closest homologue. The concentration of actinium in the mixture of rare earths was achieved by tedious fractional precipitations, whereby actinium follows lanthanum, but the



**Figure 2.** Institut du Radium (about 1931). From left to right, Sonia Cotelle, Marguerite Perey, Jukowack, and Tcheng-Da-Tchang.



**Figure 3.** The Actinium Series in 1935. Short-lived intermediates between  $^{223}\text{Ra}$  and  $^{211}\text{Pb}$  are discarded. (Courtesy, J.-P. Adloff).

separation of the two elements was never complete. A few grams of oxides containing 1 to 2 mg. of actinium had been obtained at the Institut du Radium, an amount contained in about 10 tons of uranium. (3)  $^{227}\text{Ac}$  was considered rayless for years. It could be detected only by the radiations of its decay products. In the second edition of her monumental *Radioactivité* Marie Curie stated, "Actinium itself does not emit an observable radiation," and the half-life of  $^{227}\text{Ac}$  is given as "about 10 years" [12]. The inability to observe  $\beta$ -rays from  $^{227}\text{Ac}$  had led to speculations about a radioactive decay mode by e-creation, the reverse of electron capture, in which the  $\beta$ -ray would be retained in an electronic orbital of the daughter atom. Despite all such difficulties, research on actinium and its daughter products was pursued intensively at the Institut du Radium.

### Marguerite Catherine Perey (1909–1975) [13–16]

In October, 1929 a young woman, Marguerite Perey, was hired as a chemical technician at the Institut du Radium in Paris (Figure 2). That same year she had received her diploma at the École d'Enseignement Technique Féminine, a private but state-recognized school for technicians. She had the privilege of becoming Marie Curie's personal laboratory assistant.

From 1930 on, most of Marie Curie's experimental work dealt with the preparation of pure sources of the descendants of actinium and the magnetic spectroscopy of their  $\alpha$ -radiations. Thus, at the beginning of her career Perey was confronted with the chemistry of this tricky element and its daughter products. She was to devote most of her scientific life to the radioactive actinium family, and the first years that she spent with Madame Curie might be regarded as a premonitory sign of destiny and the first step toward a major discovery.

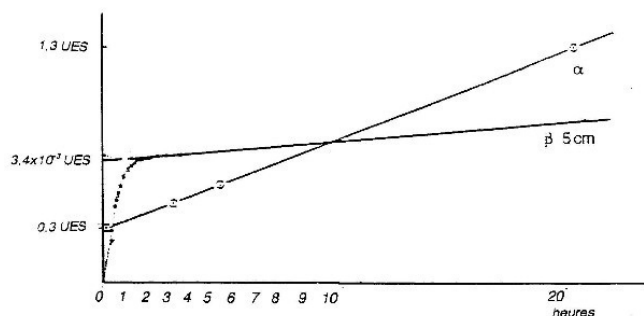
Under Curie's guidance, Perey had to learn two distinct chemical operations. First, the concentration of actinium in a mixture of rare earths was a tedious process that required dozens of repeated crystallizations and evaporations or fractional precipitations, for example, of oxalates [1]. Second, the actinium series encompasses several short-lived isotopes of the elements thorium, radium, lead, bismuth, and thallium, which had to be separated, sometimes in a matter of minutes. Figure 3 depicts a simplified scheme of the Ac family. After Marie Curie's death in July, 1934, Perey pursued her work under the direction of André Debierne, the new Director of the Institut du Radium, and Irène Joliot-Curie (1897–1956). At the Institut the interest in a concentrated source of actinium had not faded. Debierne and Joliot-Curie were both interested in the radioelement. Independently of, and unknown to each other, they asked Perey to pursue the concentration and purification of actinium. Joliot-Curie wanted to determine the precise half-life of  $^{227}\text{Ac}$ , while Debierne was involved in a mysterious search for *neo-radioelements*, by which he probably meant long-lived and chemically slightly different isotopes of radium or actinium.

### The Discovery of Actinium K

By the end of the 1930s no radiation of  $^{227}\text{Ac}$  itself had been firmly identified. The radioelement could be measured only by the rays of its daughter products (Figure 3). The first product was an isotope of thorium,  $^{227}\text{Th}$ , with atomic number 90. Hence according to the displacement laws, the parent  $^{227}\text{Ac}$  (atomic number 89) *must* be a  $\beta$ -emitter. The estimated end point of the  $\beta$ -spectrum was a few tens of keV, and such a soft radiation could not be detected unless the actinium sources were nearly carrier-free. Because actinium is always mixed with lanthanum, this condition could not be achieved, and most of the radiation was absorbed in the preparation.

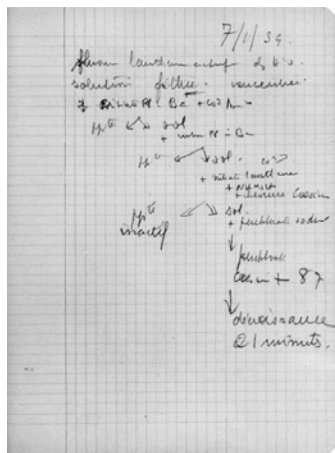
In 1935 D. E. Hull, Willard Frank Libby (1908–1980), and Wendell Mitchell Latimer (1893–1955) detected electrons emitted by actinium with a maximum energy of 220 keV [17]. This seemed very strange to Perey, who wondered if Hull's  $\beta$ -rays were not those emitted by other daughters of actinium. The observation had to be confirmed. Perey, an expert on the actinium series, knew that for this purpose it was necessary to use actinium with a minimum amount of carrier and to eliminate carefully *all* daughters of actinium. At the same time the hypothesis of e-creation that was in fashion at the Institut du Radium could be verified. Probably these reasons prompted Perey to search actinium's own  $\beta$ -radiation.

Perey's plan was to clean radiochemically a very concentrated source of actiniferous lanthanum oxide and immediately after the purification to measure the radiation of actinium before it was smeared by that of the daughters. The in-growth of short-lived  $\beta$ -emitters is governed by the slow formation of the first daughters  $^{227}\text{Th}$  and  $^{223}\text{Ra}$ , which is

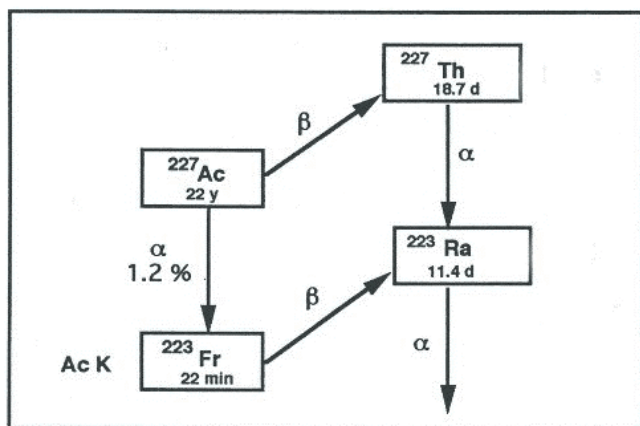


#### Growth of $\alpha$ and $\beta$ activities in freshly purified $^{227}\text{Ac}$

**Figure 4.** Growth Curves of  $\alpha$ - and  $\beta$ -Activities in Freshly Purified Actinium. The  $\alpha$ -activity of the first daughter  $^{227}\text{Th}$  increases linearly with time. The  $\beta$ -activity refers to the formation of AcK. The  $\beta$ -rays of  $^{227}\text{Ac}$  itself are not detected under the experimental conditions. UES (esu) units refer to the intensity of ionization currents. (Reference 1).



**Figure 5.** First Mention of Francium in Marguerite Pery's Notebook (January 7, 1939). AcK coprecipitated with cesium perchlorate decreases with a half-life of 21 minutes. (Courtesy, J.-P. Adloff).



**Figure 6.** The  $\alpha$ -Branching of Actinium to AcK and Closure of the Cycle. (Courtesy, J.-P. Adloff).

achieved within three months. Pery had the skill required for a fast and complete purification of actinium, and she was able to begin the measurement of the  $\beta$ -activity a few minutes after the

ultimate chemical operations. At this moment she made the crucial observation that during the first two hours the activity increased rapidly with a half-life of about 20 minutes, reached a plateau, and then increased slowly with the formation of the decay products (Figure 4). The first part of the growth curve could be extrapolated to time zero (end of the purification); at that moment the  $\beta$ -activity was nil.

Two conclusions could be drawn—first, the initial activity was not that of  $^{227}\text{Ac}$ , because it would not change with time, and second, the radiations of  $^{227}\text{Ac}$  could not be detected under the experimental conditions. Pery had used an ionization chamber with a 0.01-mm. aluminum window that would fully absorb the 220 keV  $\beta$ -rays reported by Hull *et al.* Pery concluded that the detected  $\beta$ -rays must have an energy below 80 keV, an assumption that was rapidly confirmed with a Wilson cloud chamber. Later measurements showed that the energy of the  $^{227}\text{Ac}$   $\beta$ -particles is only 45 keV. These  $\beta$ -rays were completely stopped by an absorber of 3 mg  $\text{cm}^{-2}$  surface density or were self-absorbed when actinium is mixed with rare earths or other carriers.

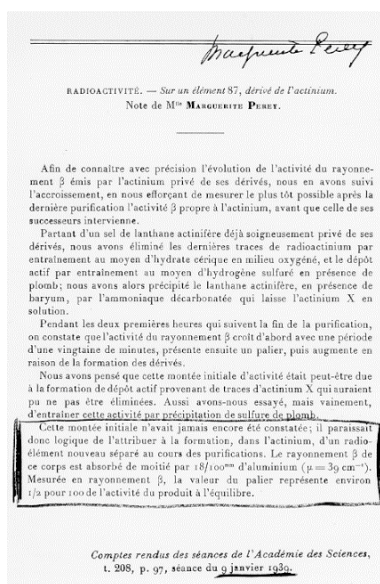
Pery's discovery was so unexpected and perplexing that it required a thorough verification before any conclusion could be drawn. It seemed likely that the new  $\beta$ -activity was that of an unidentified decay product separated during the purification and growing again in purified actinium. It was necessary to verify in which step the product was eliminated. After numerous tests it became certain that it could not be thorium, radium, lead, bismuth, or thallium. On the other hand, the product was carried by cesium perchlorate, and the activity of the precipitate decreased exponentially with a half-life of about 20 minutes (Figure 5).

The conclusion was straightforward. The new product exhibited the chemical properties of an alkali metal element, and it was readily inferred from the displacement laws that it was an isotope of element 87, eka-Cs, formed by  $\alpha$ -decay of  $^{227}\text{Ac}$ . The genesis was rapidly proven. First, the  $\alpha$ -activity of freshly purified actinium, extrapolated to time zero, had a finite value; second, the same source emitted  $\beta$ -particles with a range of 3.5 cm. in air. This was the radiation reported in 1914 by the Vienna team [11], first attributed to  $^{227}\text{Ac}$ , then to traces of  $^{231}\text{Pa}$ . Pery verified that her actinium was free of protactinium, which in any case would have been eliminated in the purification procedure.

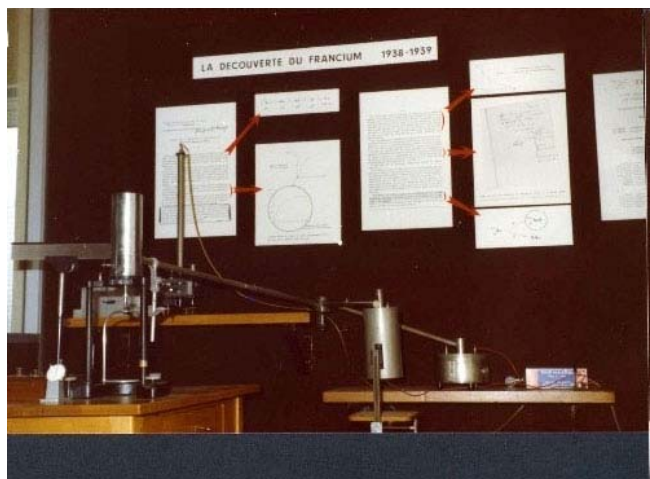
The determination of the proportion of actinium atoms decaying to eka-Cs was, of course, indispensable. In a first trial Pery extrapolated to time zero the growth curves of the  $\alpha$ - and  $\beta$ -activities of a freshly purified sample and estimated the branching at 0.6 percent. With the use of an improved ionization chamber she later revised this value to about 1 percent.

For the sake of clarity the new product needed a name. In 1904, with the proliferation of new radioactive substances, Ernest Rutherford (1871–1937) proposed assigning a letter of the alphabet to each product. The terminal product of the longest series (that of  $^{238}\text{U}$ ) became RaG. The letters H, I, and J were discarded for scriptural, phonetic, or other reasons. Eventually, Pery proposed the name *actinium K* (AcK) for the isotope of eka-Cs that she had discovered (Figure 6).

The real origin of the new product was still questionable. Pery cautiously proposed that “either actinium has a weak  $\alpha$ -branching, or it is a mixture of two isotopes, one of which decays by  $\beta$ -emission and the other by  $\alpha$ -emission” [1, 18].



**Figure 7.** First Page of Note at the Académie des Sciences Announcing the Discovery of Francium, with Marguerite Perey's signature (Courtesy, J.-P. Adloff).



**Figure 8.** Exhibition (now dismantled) of the Discovery of Francium at the Laboratory of Nuclear Chemistry at the Université Strasbourg. The equipment designed by Pierre Curie was used by Marguerite Perey and her collaborators. The  $\alpha$ - and  $\beta$ -ionization chambers are connected to an electrometer and the current is measured with a piezoelectric quartz. (Courtesy, J.-P. Adloff).

The second possibility could be eliminated by proving that  $^{223}\text{Ra}$  was the daughter of AcK. Because of the very small parent-to-daughter half-lives ratio and weak  $\alpha$ -branching, the detection of  $^{223}\text{Ra}$  after the decay of AcK was not feasible. The proof that  $^{227}\text{Th}$  and AcK beget the same daughter was based on the calculation of the energies released in both modes. The agreement, although not perfect, was indicative of the closure of the cycle, and this was confirmed experimentally several years later [19].

As a modest, 29-year-old technician without a university degree, Perey had discovered the first isotope of eka-caesium with mass number 223. No particular knowledge of fundamental science was needed, except for skill, conscientiousness, and perseverance. She had succeeded serendipitously in making a discovery that had been deliberately sought and missed by more experienced

researchers. The nuclear data that she determined are amazingly close to the most recent values.

The discovery of AcK caused some disturbance in the Institut du Radium [20]. Perey had asked for advice and independently kept her two chiefs, Debierne and Joliot-Curie, informed of the unexpected and fascinating result of her work, without ever telling either one that they were not the only investigators or sources of inspiration. Therefore, when Irène Joliot-Curie announced to Debierne that Perey had discovered eka-caesium in the course of an investigation that she, Joliot-Curie, had directed, he flew into a rage because he believed that he alone had directed Perey's work. Possibly as a consequence of this dissension, neither of the two was listed as a coauthor on Perey's publication of the discovery. This report appeared as a note in the *Comptes Rendus* presented at the Académie des Sciences by Jean Perrin on Monday, January 9, 1939 with the title "On an element 87, derived from actinium" [18] (Figure 7).

The discovery was correctly reported on March 24, 1939 in the weekly *La Lumière* by the journalist Eugène Schreider [21]. A few days later, Schreider received a letter from Jean Perrin, which required the publication of a second article on April 20. Perrin recalled that eka-Cs had been characterized for the first time in his laboratory three years earlier by Hulubei [6] from the X-ray spectrum of the element in a sample of pollucite ( $\text{H}_2\text{O} \cdot 2\text{Cs}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ ). Perrin added,

We pursue the concentration, still very small, of this element, which is certainly very stable. Therefore it is different from the fugitive element characterized in Mlle. Perey's (moreover, very interesting) research and which is probably an isotope of the element discovered by Hulubei [7].

At the time nuclear systematics was not yet sufficiently developed to prove the nonexistence of a stable or long-lived isotope of element 87; on the other hand, there was no reason to suspect that, in the midst of the radioactive elements at the end of the periodic chart, eka-Cs should be stable. Perrin's last comment was even more aberrant. He announced that Hulubei and Yvette Cauchois had also discovered in his laboratory element 93 "whose existence is certain, it exists naturally in amounts sufficient to be detected by spectroscopy, and probably it can be concentrated chemically" [7].

### Francium (Figure 8)

Once the existence of AcK had been proved, the properties of the radiations emitted by the new substance had to be determined. Perey was assisted by Marcel Lecoq, a physicist at the Institut du Radium. The results appeared in several publications between 1939 and 1943. Perey also established a new method for measuring actinium based on AcK—waiting for 2 hours for the equilibrium between the two products to be established, separating the AcK, and measuring its activity. After calibration the amount of actinium was easily determined. This method avoided the three months delay required for completing the equilibrium of actinium with its daughters. Later the procedure was routinely used for actiniferous substances and uranium minerals until the advent of  $\alpha$ -spectroscopy with solid state detectors. Perey had also patented methods for the concentration of actinium in rare earths.

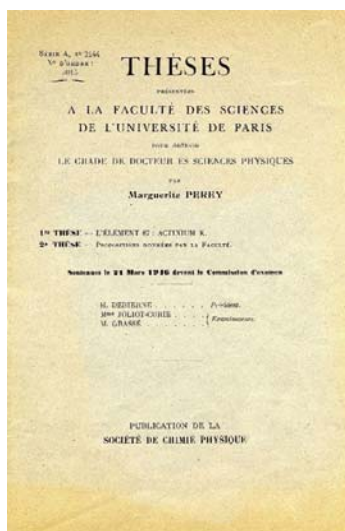


Figure 9. Cover Page of Marguerite Perey's Thesis, March 21, 1946 (Courtesy, J.-P. Adloff).

After the discovery of AcK, Perey was freed from professional work and encouraged by Debierné and Joliot-Curie to undertake university studies at the Sorbonne with a grant from the Centre National de la Recherche Scientifique (CNRS), the French establishment for scientific research. Perey's case was exceptional. She had enough material to submit a thesis but did not even possess the *baccalauréat* degree that was compulsory for registering at the university. In a first step she obtained an equivalent of the diploma by attending the preparative course for medical studies. Afterwards, from 1942 to 1945, she obtained three certificates required for the *licence* diploma. She chose the subjects of chemistry, physiology, and biology because her background in mathematics was insufficient for physics and also because of her special interest in the life sciences. She was now qualified to defend a thesis for the *Docteur ès Sciences Physiques* degree. She presented her thesis, *L'élément 87: Actinium K*, on March 21, 1946 (Figure 9).

The members of the examination board were Debierné, Irène Joliot-Curie (both apparently reconciled with each other), and the biologist Pierre-Paul Grassé (1895–1985), a member of the Académie des Sciences, who had been selected to judge the “second thesis,” usually a bibliographical review. The subject proposed by the faculty was “Labeling in biology.” Perey's mother was present at the defense; she had always been skeptical of Marguerite's discovery and was convinced that her daughter would fail! What Perey appreciated the most after the dissertation was Joliot-Curie's comment: “Today my mother [Madame Curie] would have been happy” [22].

The last line of the thesis reads: “The name Francium, Fa, is proposed for box 87.” Friedrich A. Paneth, Chairman of the International Committee for Nomenclature, had enacted very precise rules for the names and symbols of elements because of the continuing use of the names masurium and illinium instead of the correct technetium and promethium [23]. Unaware of Perey's proposal, he wrote to his French committee colleague Bertrand Goldschmidt (1912–2002):

We should like Mlle. Perey to suggest a name for 87. There is no doubt whatever that she is entitled to do so, and I think everybody will agree too that actinium K is no suitable name for the element, but only for that particular

isotope. I suppose you can easily get in touch with Mlle. Perey and explain to her that we hope to achieve an international agreement on the nomenclature of all elements which will give due credit to the real discoverers, and then ask her to let me have her suggestion for a suitable name for element 87 [24].

Informed by Goldschmidt, Perey replied to Paneth:

In the defense of my thesis on March 1946, I had suggested the name “catium” with symbol Cm because the place 87 in the periodic chart was that of the most electropositive cation. [This statement was incorrect because of relativistic effects; Dirac–Fock calculations of binding energies show that cesium is the element with the lowest ionization potential, 3.49 eV compared to 3.61 eV for eka-Cs.] I consulted M. Debierné, who considered that the name had the advantage of relying on a scientific reason. The name raised little enthusiasm and was found unesthetic. [Irène Joliot-Curie thought it was suggestive of “cat” rather than “cation.”] On the other hand, the symbol being the same as for curium, I am quite willing to give another name. M. and Mme. Joliot preferred the second name I had proposed, “Francium” with symbol Fa. I would be glad to have your advice [25].

Paneth was quite satisfied with Perey's new proposal:

I was very pleased to have your letter with the suggestion of naming element 87 “francium”, symbol Fa. I have little doubt that the name is much preferable to the one previously considered by you, for the reasons stated in your letter. It is, of course, to be understood that the name Actinium K, chosen by you years ago for the branch product in the actinium series will remain in use too, but I think we all agreed that for the element a more general name had to be found than the one designating the special member of one special series; the same as “RaF” would never have been a suitable name for the element “Polonium” [26].

The name *francium* was officially adopted without discussion, but on Goldschmidt's suggestion, Perey agreed to change the symbol to Fr. This change was also acknowledged by Paneth:

I think it is a fairly general rule in chemistry that as a symbol the first letter, or the two first letters, of the name are taken, unless they are already given to another element. So in the case of francium, I think every chemist will expect Fr to be the symbol [27].

Meanwhile, before any official decision, William F. Meggers, the National Bureau of Standards (NBS) reviser of the Welch periodic chart, had introduced the symbol Fa in the 1947 chart. Paneth commented on this decision in a letter to Perey:

The arguments put forward by Mr. Meggers in favor of Fa seem to me rather weak. The symbol of Cesium could not be Ce, and that for Rubidium Ru, because these symbols had already been given to other elements; otherwise the two first letters would have been quite naturally chosen as they were for Li and Na. As for Mr Meggers' second argument, that Fr is the usual abbreviation for France or French, seems to me just one more reason why it should also be the symbol for the element Francium even if the general habit of chemists in choosing symbols did not lead exactly to the same conclusion. The “inappropriate and unfortunate” connection (to use Mr Meggers' words) between this “very unstable form of matter” and France was established when you chose the name Francium; what



**Figure 10.** Marguerite Perey in Nice about 1971 (Courtesy, J.-P. Adloff).

else should it mean but a chemical element discovered in France? It is only natural that the symbol of the element conveys the same impression as the full name, and personally, I do not think that the life-time matters [28].

Nevertheless, Perey's suggestion of "Fa" in her printed thesis introduced some confusion for several years (*Littera scripta manet*). The 1951 Chemistry Nobel laureate Glenn T. Seaborg (1912–1999) asked Perey for clarification:

I am writing to inquire as to the symbol, which you have finally chosen to apply to element number 87, francium. It was given in your thesis and in the publication of your thesis as Fa, but I gather from Paneth's article in *Nature* that you later decided upon Fr. It seems to me that the final word on this should rest with you, and I would like very much to know your decision in order that I might use the proper symbol. I would like to congratulate you on your fine work on this element [29].

### The Thirtieth Anniversary of Francium

In 1949 Perey was appointed to a new chair of Nuclear Chemistry at the Université Strasbourg, and she founded a laboratory at the Centre de Recherches Nucléaires. During her work on actinium she had already felt the first signs of radiation sickness. The disease progressed ineluctably with increasing suffering. From 1959 on, Perey was constrained to cease progressively her activities and settled in Nice (Figure 10).

Perey always considered AcK as her own. On being informed of the existence of nine artificial isotopes of francium with half-lives shorter than that of the 21 minutes for  $^{223}\text{Fr}$ , she wrote:

I was not aware that my francium now had 9 brothers and sisters. What a large family of short-sized members which will soon celebrate its 30 years! And my eldest still remains the tallest! [30].

This is still true today although the "family" has increased to 33 isotopes with one single natural representative,  $^{223}\text{Fr}$ . The thirtieth anniversary of the discovery was celebrated in Strasbourg on March 21, 1969 when Perey, the sole survivor of

the 18 French discoverers of elements, visited her laboratory for the last time. A few months earlier she recalled the event:

I can assure you that at this time, 30 years ago, I had to contend with severe difficulties. I was certain that a new substance existed that was generated by actinium and that it should have chemical properties typical of the alkali metals. In that case it would be formed by alpha-ray emission of actinium. You can imagine the means at my disposal: use of an electrometer, followed by Geiger–Müller counters which could scarcely detect 100 to 120 counts per minute! I had to do all the work alone, without interruption from 9:00 to 23:00 or midnight. The occasional presence of some persons was either an encouragement or a hindrance. By the end of the [1938] Christmas vacation I had thought a great deal about my project and had drawn up a plan for working. When I saw Debierne, I asked for a 3-week leave during which I could work freely on my ideas and promised to abandon my project if, at the end of this time, I was unable to provide proof for the existence and origin of the presumed new element. After an initial flat refusal, he reluctantly consented, stating that the idea was stupid and would end in failure. So I started to work with all the intensity and perseverance I could apply, and fifteen days later the results and proofs for the existence were at hand. In January 1939 my first paper on the existence of element 87 was presented at the Académie des Sciences in Paris. The announcement of the new element was basely criticized by Jean Perrin, who considered the substance as an isotope of the stable element moldavium. You can hardly imagine how many difficulties I encountered in the course of this work. That's quire normal, but many obstacles continued to arise after the project was completed. Moreover, I was only 29 years of age and held only the equivalent of a bachelor's degree in chemistry. In my situation all this was a heavy burden for me. Even if the period following my identification of francium brought certain honors, I also went through moments of tears and deceptions caused by vile traits of human character: manifestations of baseness and perfidy.... Nonetheless, I consider that, even in the course of a difficult life, God has graciously provided me with a sense of understanding for all of the contingencies in which I was involved and that He gave me the strength to continue, even in times of great illness [31].

Beginning in 1973 Perey spent her time in hospitals. She died on May 13, 1975.

### Conclusion

Perey's francium, the *last element* to be discovered in nature resounded as an echo of polonium, found by Pierre and Marie Curie in 1898 [32]. Before francium, the previously discovered natural elements were hafnium in 1923 and rhenium in 1925. Francium is also the *last radioelement* found in nature, following protactinium (element 91), discovered in 1919 by Otto Hahn and Lise Meitner (1878–1968) [33], and it is the rarest element with an amount of only 550 g. in the entire earth's crust, compared, for example, with 7400 tons for the Curies' polonium.

In 1939 the last two vacant positions in the periodic chart were those of the rare earth element 61 and of element 85, eka-I. The latter could possibly exist in a weak  $\beta$ -branching of a polonium isotope in the natural radioactive families or a weak  $\alpha$ -branching of francium. Searches for such branchings were negative until 1953 when Earl K. Hyde discovered that  $^{223}\text{Fr}$  itself decays by  $\alpha$ -emission with a 0.02 percent branching into

$^{219}\text{At}$ , the longest-lived natural isotope of element 85, with a half-life of 50 seconds [34]. The  $\alpha$ -particle energy and the branching ratio of AcK were measured by Jean-Pierre Adloff, who found 5.34 MeV and 0.06 percent, respectively [35]. Thus, *stricto sensu*, astatine is a natural radioelement; however, because of the very small branchings and the short half-lives of the natural isotopes, astatine is considered an artificial one. Nevertheless, the close link between the natural eka-Cs (Fr) and eka-I (At) elements remains a pleasant curiosity.

**Acknowledgment.** References 24–29 and Figures 1 and 2 are reproduced from the Perey Archives collected by Jean-Pierre and Madeleine Adloff, collaborators of Marguerite Perey, and transferred to the Physics Archives of the Université Louis Pasteur, Strasbourg (Courtesy, Sébastien Soubiran, Archives scientifiques, Mission culture scientifique et technique de l'Université Louis Pasteur, 7 rue de l'Université, 67100 Strasbourg, France).

## References and Notes

- Perey, M. L'élément 87. *J. Chim. Physique* **1946**, *43*, 152–168.
- Fontani, M. The twilight of the naturally-occurring elements: moldavium (Ml), sequanium (Sq) and Dor (Do). 5th International Conference on the History of Chemistry, Chemistry, Technology and Society, Estoril & Lisbon, Portugal, September 6–10, 2005 (<http://Siche-portugal.ulusofona.pt/paperslist.asp>).
- Trimble, R. F. What Happened to Alabamine, Virginium and Illinium? *J. Chem. Educ.* **1975**, *52*, 585. Virginium (Vi) and Alabamine (Ab) still appeared in the 1941 edition of the Welch Scientific Company periodic chart of the elements.
- Herszfinkiel, H. Sur les éléments de numéros atomiques 85 et 87. *Compt. Rend.* **1927**, *184*, 968–970.
- Hulubei, H. Recherches relatives à l'élément 87. *Compt. Rend* **1936**, *202*, 1927–1930. Hulubei went to Paris in 1927 with a fellowship at the Sorbonne's Laboratoire de Chimie Physique. In 1933 he received his doctorate under Jean Perrin's supervision in X-ray spectroscopy, a field in which he became a renowned authority. During World War I he was a fighter pilot for the French Air Force. He received awards from the Académie des Sciences, to which he was elected as a *correspondant*. In 1940 he was appointed Professor of Physics at the University of Bucharest, and in 1949 he founded the Romanian Institute of Atomic Physics. He was a close collaborator of Yvette Cauchois (1908–1999), also a leader in X-ray spectroscopy. She succeeded Jean Perrin in the chair of Chimie Physique in 1953 and became Director of the associated laboratory.
- Hulubei, H. Nouvelles recherches sur l'élément 87 (Ml). *Compt. Rend.* **1937**, *205*, 854–857.
- Schreider, E. La découverte de l'élément 87 de la classification périodique des éléments. Quelques précisions du professeur Jean Perrin. *La Lumière* **April 20, 1939**, 624.
- Adloff, J.P. The Centennial of a Controversial Discovery: Actinium. *Radiochim. Acta* **2000**, *88*, 123–127.
- Hahn, O. Ein kurzlebiges Zwischenprodukt zwischen Mesothor und Radiothor. *Phys. Z.* **1908**, *9*, 246.
- Hahn, O. *Vom Radiothor zur Uranspaltung*; Friedrich Vieweg: Braunschweig, 1962; pp 101–102.
- Meyer, St.; Hess, V. F.; Paneth, F. A. Neue Reichweitenbestimmungen an Polonium, Ionium und Actiniumpräparaten. *Sitzungsber. Akad. Wissensch. Wien* **1914**, *123*, 1459–1488.
- Curie, M. *Radioactivité*; 2nd ed.; Hermann: Paris, 1935; p 447. Published posthumously, this treatise was in print on Curie's death (July 4, 1934).
- Kauffman, G. B.; Adloff, J.-P. Marguerite Perey and the Discovery of Francium. *Educ. Chem.* **1989**, *26*, 135–137; reprinted in *Chemists through the Years: Part II*; Servant, D., Ed.; "Chemistry, Industry and Society" Series; The Royal Society of Chemistry: London, England, 1994; pp 152–154.
- Kauffman, G. B.; Adloff, J.-P. Marguerite Catherine Perey (1909–1975). In *Women in Chemistry and Physics*; Grinstein, L. S.; Rose, R. K.; Rafailovich, M. H., Eds.; Greenwood Press: Westport, CT, 1993; pp 470–475.
- Kauffman, G. B.; Adloff, J.-P.; Niinistö, L. Marguerite Perey ja radioaktiivisen frankiumin löytö luonnosta (Marguerite Perey and the Discovery of Naturally Occurring Radioactive Francium). *Kemia-Kemi* **2000**, *27*, 231–233 (in Finnish).
- Adloff, J.-P.; Kauffman, G. B. Marguerite Catherine Perey (1909–1975). In *Out of the Shadows: Contributions of 20th Century Women to Physics*; Byers, N.; Williams, G., Eds.; Cambridge University Press: Cambridge, England, 2005; pp 371–384.
- Hull, D. E.; Libby, W. F.; Latimer, W. M. The Beta-ray of Actinium. *J. Am. Chem. Soc.* **1935**, *57*, 1649–1652. This report is at the origin of Perey's discovery. She kept the reprint on hand on the laboratory shelf as shown by its partial deterioration by acids and other chemicals. The extent of the document's contamination was never measured.
- Perey, M. Sur un élément 87, dérivé de l'actinium. *Compt. rend.* **1939**, *208*, 97–99. Most of this paper appears in English translation in Davis, H. M. (revised by Seaborg, G. T.) *The Chemical Elements*; 2nd ed.; Science Service: Washington, DC, 1959; pp 26–28.
- In 1947 Marcel Guillot and Perey, using a photographic emulsion method, identified the same daughters of actinium regardless of whether they arose from the  $\alpha$ - or  $\beta$ -branch of actinium (Guillot, M.; Perey, M. Sur la descendance radioactive de AcK. *Compt. Rend.* **1947**, *225*, 330–332). It was not until 1955 that Perey and Jean-Pierre Adloff were able to observe the growth of  $^{223}\text{Ra}$  in AcK and to confirm definitively the closure of the AcK cycle (Perey, M.; Adloff, J.-P. Sur la descendance du francium. *J. Physique* **1956**, *17*, 545–547).
- Goldschmidt, B. *Atomic Rivals*; Rutgers University Press: New Brunswick, NJ, 1990; pp 18–19.
- Schreider, E. Comment on a découvert le 87ème corps chimique simple. *La Lumière* **March 24, 1939**, 620.
- Perey, M. En souvenir de Madame Curie. Remembrance at the occasion of the centenary of Marie Curie, Archives J.-P. Adloff.
- Paneth, F. A. The making of the missing chemical elements. *Nature* **1947**, *159*, 8–12.
- Paneth, F., letter to B. Goldschmidt, April 26, 1946.
- Perey, M., letter to F. A. Paneth, June 27, 1946.
- Paneth, F., letter to M. Perey, July 9, 1946.
- Paneth, F., letter to M. Perey, November 27, 1946.
- Paneth, F., letter to M. Perey, March 10, 1947.
- Seaborg, G.T., letter to M. Perey, November 4, 1947.
- Perey, M., letter to J.-P. Adloff, February 25, 1968.
- Perey, M., letter to J.-P. Adloff, November 21, 1968.
- Curie, P.; Curie, M. Sur une substance nouvelle radio-active, contenue dans la pechblende. *Compt. Rend.* **1898**, *127*, 175–178.
- Sime, R. L. The Discovery of Protactinium. *J. Chem. Educ.* **1986**, *63*, 653–656.
- Hyde, E. K. The Alpha-branching of AcK and the Presence of Astatine in Nature. *Phys. Rev.* **1953**, *90*, 267–220.
- Adloff, J.-P. Evolution de l'activité  $\alpha$  d'une source d'actinium K (Fr 223). *Compt. Rend.* **1955**, *240*, 1421–1423.