A Short History of Polonium and Radium

by Jean-Pierre Adloff

In 1897 at the age of 30, Maria Skłodowska, who had married Pierre Curie in 1895, concluded her studies at the Sorbonne in Paris and was thinking of a subject for a thesis. X-rays, discovered by Wilhelm Conrad Röntgen in 1895, were still a topical question, but had lost the charm of novelty. On the other hand, the uranic rays, discovered in 1896 by Henri Becquerel, raised a puzzling problem. Uranium compounds and minerals appeared to maintain an undiminished ability to blacken a photographic plate over a period of several months. What was the source of this inexhaustible energy that apparently violated the Carnot principle that energy can be transformed but never be created or destroyed? Pierre Curie, already a famous physicist for his work on magnetism and crystal symmetry, had a feeling that the phenomenon was quite extraordinary, and he helped his wife reach a decision in her choice of thesis topic. Marie Curie, in a biography of Pierre Curie, confirmed, "we felt the investigation of the phenomenon very attractive, so much the more so as the topic was quite new and required no bibliographical research."

An illustration from Vanity Fair magazine, 1904 (Library of Congress).

After initial excitement, interest in the new rays had faded rapidly. One reason was the proliferation of false or doubtful observations of radiation similar to uranic rays in a variety of substances. The topic was moribund when Marie Curie entered the scene. However, within eight months in 1898 she discovered two elements, polonium and radium, founding a new scientific field—radioactivity. This short history of the discoveries is retraced from three laboratory notebooks in which one can distinguish the writings of Pierre and Marie (Adloff 1998) and from three notes published in the *Comptes Rendus de l'Académie des Sciences (C.R. Acad. Sci. Paris)*.

In addition to blackening a photographic plate, uranic rays rendered air conductive for electricity. This later property was much more amenable to quantitative measurement. Becquerel had used electroscopes, but the measurements were unreliable. At this point, little progress would have been made without the genius of Pierre Curie. In 1880, together with his brother Jacques, he had discovered piezoelectricity (i.e., the production of electric charges when pressure is applied to hemihedral crystals such as quartz). He invented a device by which the charges produced by uranium in an ionization chamber were compensated for by opposite charges in known amounts produced by applying a weight to a leaf of quartz. The compensation was followed by a second invention, the quadrant electrometer. The emission of uranic rays could now be quantified from the weight and the time required for compensation of the charges produced in the ionization chamber.

The "Curie Laboratory": left, chemistry bench; right, ionization chamber and electrometer.

Marie Curie's First Publication: 12 April 1898

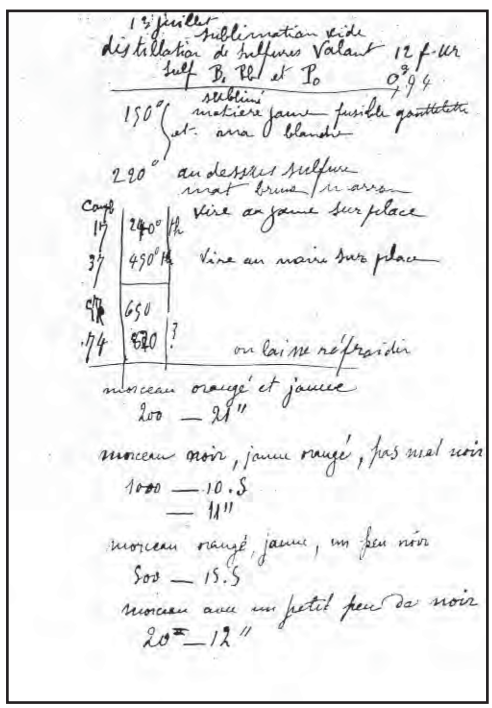
Marie Curie's strategy is clearly expressed in her first note published on 12 April 1898 in the *Comptes Rendus de l'Académie des Sciences*: "I have searched [to see] if substances other than uranium compounds render air conducting for electricity" (Curie, M. 1898). Beginning on 11 February 1898, she tested all samples at hand or borrowed from various collections, including a large number of rocks and minerals, taking the activity of metallic uranium as a reference. She found that all compounds and minerals that contained uranium were active and that pitchblende, a massive variety of uraninite from the Joachimasthal mine in Austria, as well as chalcolite, a natural uranium phosphate, were more active than metallic uranium itself. Marie Curie noted, "This fact is quite remarkable and suggests that these minerals may contain an element much more active than uranium." Her hypothesis was immediately confirmed: "I have prepared chalcolite with pure products; this artificial chalcolite is not more active than other uranium salts." She then concluded that an unknown element exists only in the uraniferous minerals that are more active than uranium. At this stage, the hunt for the supposed element became a matter of paramount importance and urgency. Pierre Curie was fascinated by Marie's findings: On 18 March he abandoned his own research projects and joined his wife in the venture.

In the course of the systematic search of Becquerel rays, Marie Curie also discovered, on 24 February, that thorium compounds were also active. However, the German physicist Gerhardt Schmidt had observed the emission several weeks earlier.

The Discovery of Polonium: 18 July 1898

The research on uranic rays now turned from physics to chemistry. It became necessary to separate and identify a substance whose chemical properties were unknown. However, the hypothetical element could be followed by tracing its radioactivity. Marie Curie explained the process: "The method we have used is a new one for chemical research based on radioactivity. It consists of separations performed with the ordinary procedures of analytical chemistry and in the measurement of the radioactivity of all compounds separated. In this way, one can recognize the chemical character of the radioactive element sought; the latter is concentrated in fractions which become increasingly radioactive in the course of the separation." Neither Marie nor Pierre were chemists, so they were assisted by Gustave Bémont, who was in charge of practical training for students at the Parisian Ecole Municipale de Physique et Chimie Industrielle.

On 14 April, the trio began research on pitchblende, which was two and a half times more active than uranium. Several procedures were used in parallel runs by precipitations with various reagents and sublimations of solid deposits, whereby the active substance accompanied primarily bismuth, from which it could be progressively separated. On 27 June, Marie Curie precipitated sulfides from a solution containing lead, bismuth, and the active substance. She underlined the result in her notebook: the solid was 300 times more active than uranium. On 18 July, Pierre Curie obtained a deposit 400 times more active than uranium. The Curies carefully verified that "compounds of all elements, including those of the rarest substances were not active."



First mention of polonium, "Po" in the laboratory notebook of Pierre and Marie Curie, 13 July 1898.

A Short History of Polonium and Radium

On 18 July 1898, Pierre and Marie Curie wrote to the *Comptes Rendus de l'Académie des Sciences*, "On a new radio-active substance contained in pitchblende." "We believe that the substance we recovered from pitchblende contains a heretofore unknown element, similar to bismuth in its analytical properties. If the existence of this new metal is confirmed, we propose that it be named polonium in honor of the native land of one of us" (P. Curie and M. Curie 1998). The symbol Po, written by Pierre Curie, appears in the notebook on 13 July. The name polonium had a provocative significance because Poland had disappeared as a state in 1795, being divided between Prussia, Russia, and the Austrian Empire.

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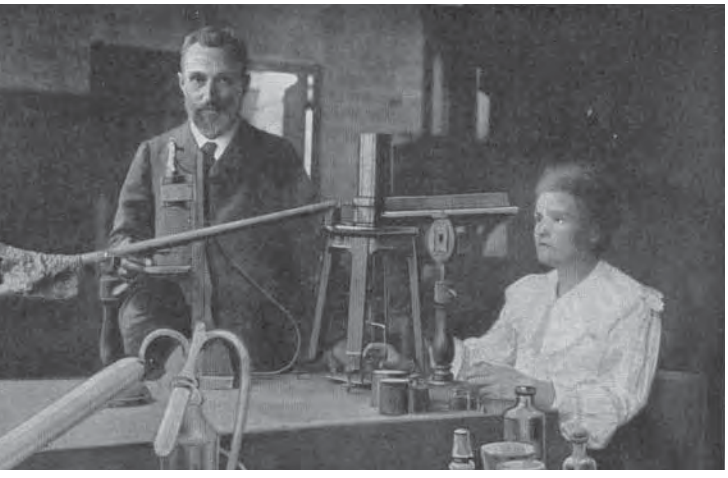
The publication signed both by Pierre Curie (as first author) and Marie Curie, was based on experiments performed from 9 April to 16 July. The title is historic: It proclaims that the search for the element more active than uranium was successful, and the word *radio-active* appears for the first time (The Curies dropped the hyphen the following year). The announcement of a new element that remained invisible and was identified solely on the basis of its emission of "uranic rays" was unique in the history of chemistry. It was customary that no such claim was considered valid until a pure substance had been isolated, the atomic weight of the element had been determined, and its spectral lines had been measured. Eugène Demarçay, a recognized authority in spectroscopy, examined the spectrum of the new element, but to the Curies' disappointment he could not distinguish any new characteristic lines. The authors admitted, "This fact does not favor the idea of the existence of a new metal."



Pierre and Marie Curie handling the electrometer.

The isolation of polonium from uranium had been accomplished although the Curies were unaware of the relationship between the two elements. They considered the entire material as a mixture. They knew nothing of radioactive decay. In this sense it was purely a matter of chance since the experiments were performed within three months, a relatively short time with respect to the 138-day half-life of polonium.

It was only a few years later that the authors noticed with astonishment and great perplexity that polonium was progressively disappearing, still unaware of its half-life. They were preoccupied with the authenticity of polonium for several years, and with their customary honesty they did not hide their doubts. In 1899, Marie Curie still raised the question: "Is polonium, which exhibits the lines of bismuth, really a new element or simply bismuth activated by the radium contained in pitchblende?" The doubt persisted for several years (Adloff 2007). Eventually, in 1910 Marie Curie and André Debierne separated from several tons of residues of uranium ores a final product that weighed 2 mg and contained about 0.1 mg of polonium. The spark spectrum of this sample revealed for the first time a few lines characteristic of the element. The position of polonium in the periodic table was not assigned by the discoverers, but the new element could obviously be placed to the right of bismuth as "eka-tellurium," with atomic number 84.

The note in the *Comptes Rendus* concluded the short story of polonium for several years. Marie Curie maintained a strong sense of ownership for the element, which she defended with considerable emotion and vehemence. In a sense she was correct: the subsequent discoveries of the atomic nucleus, artificial radioactivity, and fission were all performed with her polonium.

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The Discovery of Radium: 26 December 1898

The Curies laboratory notebook has no record from July to 11 November. The Curies suspected the presence of a further radioactive element in the pitchblende, which behaved like "nearly pure barium." Their hypothesis was confirmed in three steps. First, they verified that "normal" barium was inactive. Second, they found that a radioactive substance could be concentrated by fractional crystallization from barium chloride contained in pitchblende. They pursued this operation until the activity of the chlorides was 900 times greater than that of uranium. Their third and last argument was decisive. This time the spectroscopic analysis was successful. Demarçay observed in the spectrum of radioactive barium chloride several lines that could not be assigned to any known element and whose intensity increased with the radioactivity. The Curies concluded, "We think this is a very serious reason to believe that the new radioactive substance contains a new element to which we propose to give the name radium." They added, "the new radioactive substance very likely contains a large amount of barium, nevertheless, the radioactivity of radium must be enormous." The name, "radium," followed by a question mark appears in the notebook on 18 November.

At that time, the authors had used up their supply of pitchblende and were aware that vast amounts or raw material would be necessary in order to prepare "visible," or at least much larger quantities of, the two new elements. In December 1898, the Austrian government offered the Curies a first batch of 100 kg of uranium-free residue from the treatment of the Joachimsthal pitchblende. The authors acknowledged that "this shipment will greatly facilitate our research."

The determination of the atomic mass of radium became an obsession for Marie Curie. On 21 July 1902, she obtained the value 225±1 (now known to be 226.0254) on a self-luminous sample of 0.120 g of radium chloride with a radium barium ratio of 10^6, which was one million times more active than uranium.

With the foregoing discovery of polonium, the Curies had oddly enough begun with the most difficult part of the work. In its own right, radium had outstanding advantages: its half-life is 1600 years; its concentration in the ores was about 5000 times greater than that of polonium; it is a true analog of barium, from which it can be separated; and it could be readily assigned its place in the periodic table.

On 12 June 1903, Marie presented her thesis, "Researches on Radioactive Substances," at the Sorbonne. Later that year she shared the Nobel Prize in Physics with Pierre Curie and Henry Antoine Becquerel.

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